Chemical Sensors in Plastic Optical Fibers

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Abstract—**Plastic Optical Fibers (POFs) are especially advantageous due to their excellent flexibility, simple manufacturing and handling procedures, great numerical aperture, large diameter, and the fact that plastic is able to withstand smaller bend radii than glass. Sensors based on POFs and Molecularly Imprinted Polymers (MIPs) are presented in the selective detection of different analytes. The developed POF-MIP sensors represent a simple approach to low-cost sensing. In this work we have recalled a chemical sensor for furfural (2-FAL) detection in power transformer insulating oil, with a Limit Of Detection (LOD) of about 4µM.**

Keywords-plastic optical fibers; chemical sensors; molecularly imprinted polymers; optical fiber sensors.

I. INTRODUCTION

Surface Plasmon Resonance (SPR) is a very sensitive method for determining refractive index variations at the interface between a metal layer and a dielectric medium. Thus, it is a transduction technique particularly suitable for marker free sensors, in which the dielectric is a receptor layer with refractive index depending on its interaction with a particular substrate. In the scientific literature, several review papers describe plasmonic sensor platforms and their applications [1]-[6].

Jorgenson et al. realized SPR sensors in optical fibers without prisms [7], in which the metal layer was directly deposited on the core of an optical fiber. The SPR sensors in optical fiber allow for remote sensing and for reduced dimension and price of the whole sensor system. At the beginning, the optical fibers employed were made of glass, but more recently plastic or special optical fibers have been used too [7]-[17]. The Plastic Optical Fibers (POFs) present exceptional flexibility, simple manipulation, large numerical aperture, big diameter. Also, they are able to withstand smaller bend radii than glass fibers. Therefore, POFs are particularly advantageous for the realization of low-cost SPR sensors [16]. SPR sensors based on optical fibers show a noticeably high sensitivity, due to the fact that they are able to detect even small variations of refractive index of the medium (dielectric) in contact with the metal layer [18]-[21]. When biological or artificial receptors are present at the metal-dielectric interface, they selectively capture the analyte present in the sample under test, and a local variation of the dielectric's refractive index in contact with the metal film is produced.

Different structures have been proposed for SPR sensors based on optical fibers [5]. D-shaped POF platforms have been successfully developed by our research group for different analytes and different receptors such as antibodies, aptamers and Molecularly Imprinted Polymers (MIP) too [22]-[28].

The flat part of the D-shaped platform is suitable for an easy deposition of the receptors, in particular MIPs, and makes it possible to perform the determination in a drop, instead of requiring complex flux devices. It has been shown that MIPs are easily produced over gold by in-situ polymerization, forming thin and firm receptor layers, which are suitable for SPR detection by the D-shaped POF platforms [24]-[28].

The D-shaped POF platforms are obtained by a hand polishing procedure, which could lead to a somewhat irreproducible morphology of the D-shaped region (roughness and total depth). Previous investigations showed that this could strongly influence the performance of the platform [29][30].

MIPs are synthetic receptors with many favorable aspects with respect to bio-receptors, such as an easier and faster preparation, the possibility of application outside the laboratory, for example under environmental conditions, a longer durability [31][32].

The advantage of the MIPs combined with SPR D-shaped POF platform is that they can be directly formed on a flat gold surface by depositing a drop of prepolymeric mixture directly over gold film, spinning by a spin coater machine and in situ polymerization [24]-[28], without modifying the surface (functionalization and passivation), as needed for the bio-receptors [22][23]. Besides, their refractive index can in principle be modulated in order to be suitable for the SPR transduction.

Taguchi et al. presented a different interesting approach for Bisphenol A (BPA) detection, exploiting molecularly imprinted nanoparticles combined with a slab optical waveguide [33]. This approach is similar to that used in the Kretschmann configuration but exploiting optical fibers combined with a slab waveguide.

In this work, we reported as the combination of a D-shaped POF and an MIP receptor is an effective way to obtain a highly selective and sensitive SPR optical chemical

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sensor. Several examples of applications of this optical chemical sensor have been demonstrated, as for example the selective detection of trinitrotoluene (TNT), for security applications [24], of furfural (furan-2-carbaldehyde) and dibenzyl disulfide (DBDS) in power transformer insulating oil, for industrial applications [25][28], of L-nicotine [27] in clinical applications, and perfluorinated alkylated substances (PFAs) in environmental monitoring applications [26].

The rest of the paper is structured as follows. In Section 2, we have presented an optical platform based on plastic optical fibers. In Section 3, we have reported a particular synthetical receptor: the Molecularly Imprinted Polymer. In Section 4, we have illustrated an example of a chemical-optical sensor based on an SPR-POF platform combined with an MIP receptor. We have concluded the work in Section 5.

II. SPR-POF PLATFORM

The D-shaped POF platform was realized as described in [16], the size of the POF is 980 µm of core (1 mm in diameter). Summarily, our SPR platform is made by removing the cladding of POF (along half circumference), spin coating a buffer layer on the exposed core and finally sputtering a thin gold film [16]. Figure 1 shows the SPR-POF sensor and the outline of the manufacturing steps. The final length of sensing region is about 10 mm. The photoresist layer is about 1,500 nm thick and the gold film is about 60 nm, presenting a good adhesion to the substrate too.

The buffer layer is made of photoresist (Microposit S1813), with a refractive index greater than that of the POF's core (PMMA). This buffer layer improves the performances of the SPR sensor and the gold film adhesion on the platform.

The selectivity is obtained by placing a specific receptor (for example MIP) for the considered analyte in tight contact with the gold surface (see Figure 1).

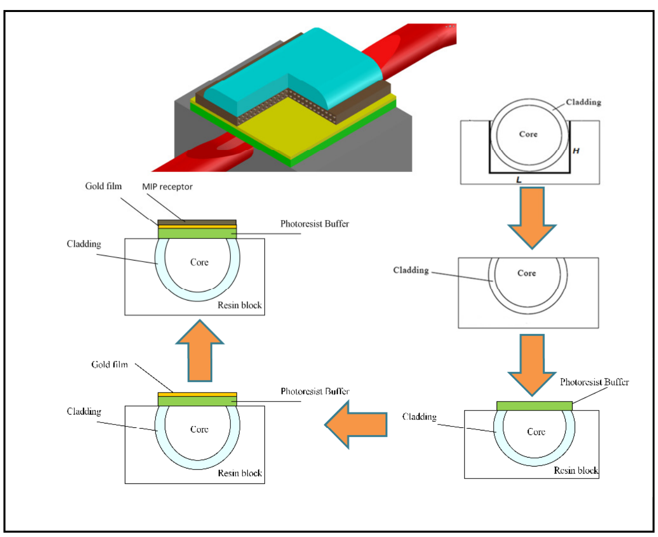

Figure 1. SPR sensor platform based on D-shaped POF.

The experimental setup consists of a halogen lamp (HL–2000–LL, Ocean Optics) illuminating the optical chemical sensor and a spectrum analyzer (USB2000+UV–VIS spectrometer, Ocean Optics) connected to a computer, as shown in Figure 2. The spectral emission of the lamp ranges from 360 nm to 1700 nm and the spectrometer is sensitive from 300 nm to 1050 nm.

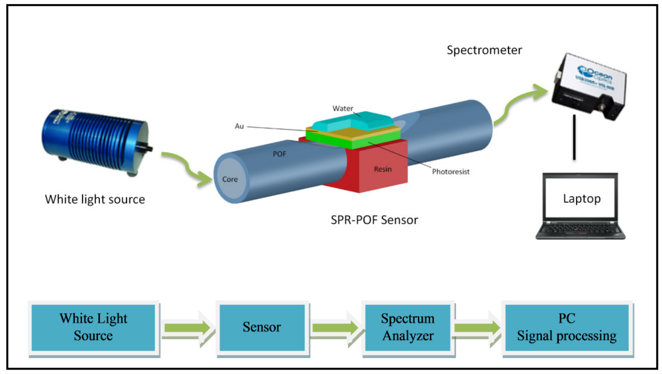

Figure 2. Experimental setup.

Usually, in the bio-chemical applications, a small amount of solution with analyte (about 50 µL) was dropped over the sensing area (MIP layer, the chemical receptor) and the spectrum recorded after about ten minutes incubation. The transmission curves along with data values were displayed online on the computer screen and saved with the help of advanced software provided by Ocean Optics. Each experimental value is the average of 5 subsequent measurements. The signal processing is obtained by Matlab and OriginPro 8.5 software.

III. MIP RECEPTORS

For the characterized optical chemical sensors [24]-[28], based on SPR-POF-MIPs, the MIP receptor layer has been obtained by three simple steps (see Figure 3).

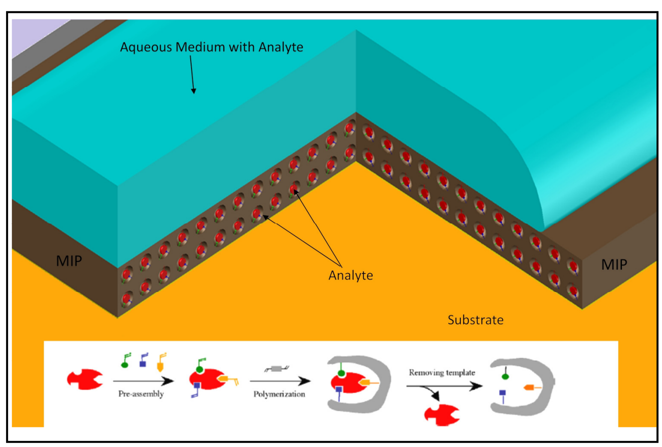

Figure 3. MIP receptor layer outline.

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In particular, we have used these steps:

1) About 50 µL of the prepolymeric mixture were dropped over the flat optical sensing region (D-shaped area) and spun for 1 min at about 700 rpm, by a spin coater machine;

2) Thermal polymerization was then carried out for 16 h at 80 °C, by oven;

3) The template was extracted by repeated washings with 96% ethanol.

Figure 3 shows the outline of the MIP receptor layer with a summary of these manufacturing steps (the porous solid obtained by polymerization of the aggregate substrate-coordinating monomers after extraction of the template from the selective site).

IV. AN EXAMPLE OF SPR-POF-MIP SENSOR

As an example, we report on the results of the exploitation of an MIP receptor on a D-shaped POF for furfural detection in power transformer insulating oil. Furfural (2-FAL) has been considered among several furanic compounds possibly present in used transformer oils, since it is usually the most prominent component of paper decomposition in power transformer [28].

The gold planar surface over the D-shaped POF (SPR active surface) was washed with ethanol and then dried in a thermostatic oven at 60 °C prior to depositing the sensing layer, a specific MIP layer. The prepolymeric mixture for MIP was prepared according to the classical procedure reported in [28] with only slight modifications. Divinylbenzene (DVB), the cross-linker, was also the solvent in which the functional monomer (that is, methacrylic acid, MAA), and the template, furfural (2-FAL) are dissolved [25][28].

Figure 4 shows the spectra of the SPR-POF-MIP sensor for 2-FAL detection, where at about 860 nm a red-shift is present for increasing concentration of analyte (2-FAL) from 0 ppm to 0.193 ppm.

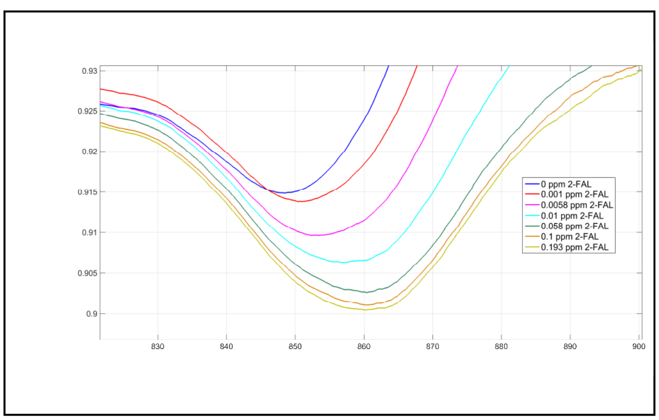

Figure 4. SPR spectra obtained for different concentrations of 2-FAL in oil.

The shift of resonance wavelength indicates that the refractive index in contact with the gold surface is increased. The dependence of the minimum wavelength on the 2-FAL concentration is evident.

Figure 5 shows the dose response curves for 2-FAL (ppm) in oil, in semi-log scale, and the Hill fitting to the experimental data, obtained by the red shift resonances shown in Figure 4.

Figure 5 shows that the experimental data are well fitted by the Hill equation, and, from the Hill parameters, we obtained a sensitivity at low concentration of about $6{\cdot}10^7$ (nm/M) and a Limit Of Detection of about 4 (µM) [25][34].

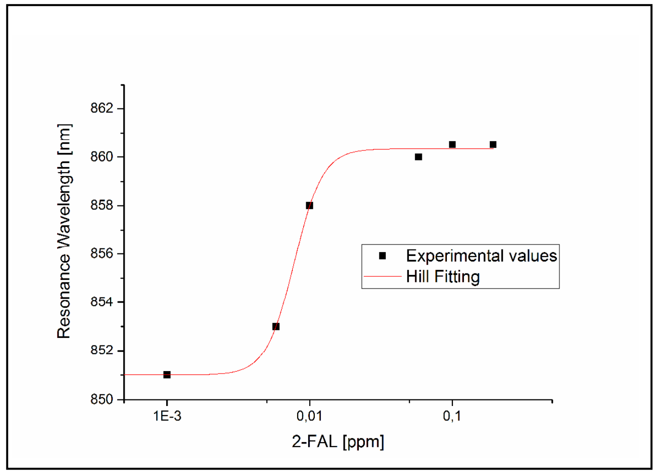

Figure 5. Resonance wavelength (nm) versus 2-FAL concentration (ppm) in oil, in semi-log scale, and Hill fitting of data.

Standardization curves like those reported in Figure 5 are generally used for chemo and biosensors, and their physical meaning can be linked to the fact that the absorption occurs by combination at specific sites, when the quantity of receptor sites available for the combination with the substrate is restricted [24]-[28][34].

V. CONCLUSIONS

We have reported on the ability of a low-cost SPR-POF sensor platform to be exploited in chemical applications based on MIP receptors.

The SPR-POF-MIP sensor systems are easy to use, small size and low-cost. As a paradigm, we have recalled the results for furfural detection in power transformer insulating oil.

REFERENCES

[1] J. Homola, "Present and future of surface plasmon resonance biosensors," Anal. Bioanal. Chem., vol. 377, pp. 528–539, 2003.

[2] A. Leung, P.M. Shankar, and R. Mutharasan, "A review of fiber-optic biosensors," Sens. Act B: Chem., vol. 125, pp. 688–703, 2007.

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[3] K. Anuj, R.J. Sharma, and B.D. Gupta, "Fiber-optic sensors based on surface Plasmon resonance: a comprehensive review," IEEE Sens. J., vol. 7, pp. 1118–1129, 2007.

[4] J. Homola, S.S. Yee, and G. Gauglitz, "Surface plasmon resonance sensors: review," Sens. Act B: Chem., vol. 54, pp. 3-15, 1999.

[5] C. Caucheteur, T. Guo, and J. Albert, "Review of plasmonic fiber optic biochemical sensors: improving the limit of detection," Anal and bioanal chemistry, vol. 407, pp. 3883-3897, 2015.

[6] M. C. Estevez, M. A. Otte, B. Sepulveda, and L. M. Lechuga, "Trends and challenges of refractometric nanoplasmonic biosensors: A review," Analytica Chimica Acta, vol. 806, pp. 55-73, 2014.

[7] R.C. Jorgenson and S.S. Yee, "A fiber-optic chemical sensor based on surface plasmon resonance," Sens. Act B: Chem., vol. 12, pp. 213–220, 1993.

[8] E. Klantsataya, P. Jia, H. Ebendorff-Heidepriem, T.M. Monro, and A. François, "Plasmonic Fiber Optic Refractometric Sensors: From Conventional Architectures to Recent Design Trends," Sensors, vol. 17, pp. 12, 2017.

[9] X.D. Wang and O.S. Wolfbeis, "Fiber-Optic Chemical Sensors and Biosensors (2008-2012)," Anal. Chem.," vol. 85, pp. 487-508, 2013.

[10] X.D. Wang and O.S. Wolfbeis, "Fiber-Optic Chemical Sensors and Biosensors (2013-2015)," Anal. Chem., vol. 88, pp. 203–227, 2016.

[11] D.J. Monk and D.R. Walt, "Optical fiber-based biosensors," Anal. Bioanal. Chem., vol. 379, pp. 931–945, 2004.

[12] A. Trouillet, C. Ronot-Trioli, C. Veillas, and H. Gagnaire, "Chemical sensing by surface plasmon resonance in a multimode optical fiber," Pure App. Opt., vol. 5, pp. 227-237, 1996.

[13] B.D. Gupta and R.K. Verma, "Surface plasmon resonance-based fiber optic sensors: Principle, probe designs, and some applications," Journal of Sensors, vol. 2009, pp. 1–12, 2009.

[14] M.E. Bosch, A.J.R. Sánchez, F.S. Rojas, and C.B. Ojeda, "Recent development in optical fiber biosensors," Sensors, vol. 7, pp. 797–859, 2007.

[15] A. Abdelghani et al., "Surface plasmon resonance fiber-optic sensor for gas detection," Sens. Act B: Chem., vol. 39, pp. 407–410, 1997.

[16] N. Cennamo, D. Massarotti, L. Conte, and L. Zeni, "Low cost sensors based on SPR in a plastic optical fiber for biosensor implementation," Sensors, vol. 11, pp. 11752–11760, 2011.

[17] M. Piliarik, J. Homola, Z. Manikova, and J. Čtyroký, "Surface Plasmon Resonance Sensor Based on a Single-Mode Polarization-Maintaining Optical Fiber," Sens. Actuat. B Chem., vol. 90, pp. 236–242, 2003.

[18] M. Kanso, S. Cuenot, and G. Louarn, "Sensitivity of optical fiber sensor based on surface plasmon resonance: Modeling and experiments," Plasmonics, vol. 3, pp. 49–57, 2008.

[19] Y.S. Dwivedi, A.K. Sharma, and B.D. Gupta, "Influence of design parameters on the performance of a SPR based fiber optic sensor," Plasmonics, vol. 3, pp. 79–86, 2008.

[20] M. Iga, A. Sek, and K. Watanabe, "Gold thickness dependence of SPR-based hetero-core structured optical fiber sensor," Sens. Act B: Chem., vol. 106, pp. 363–368, 2005.

[21] A.K. Sharma and B.D. Gupta, "On the sensitivity and signal to noise ratio of a step-index fiber optic surface plasmon resonance sensor with bimetallic layers," Opt. Commun., vol. 245, pp. 159–169, 2005.

[22] N. Cennamo et al., "An innovative plastic optical fiber based biosensor for new bio/applications. The case of celiac disease," Sens. Act. B: Chem., vol. 176, pp. 1008–1014, 2013.

[23] N. Cennamo et al., "An easy way to realize SPR aptasensor: A multimode plastic optical fiber platform for cancer biomarkers detection," Talanta, vol. 140, pp. 88–95, 2015.

[24] N. Cennamo et al., "Sensors based on surface plasmon resonance in a plastic optical fiber for the detection of trinitrotoluene," Sens. Act. B: Chem., vol. 118, pp. 221-226, 2013.

[25] N. Cennamo et al., "Markers detection in transformer oil by plasmonic chemical sensor system based on POF and MIPs," IEEE Sens. J., vol. 16, pp. 7663-7670, 2016.

[26] N. Cennamo et al., "A Molecularly Imprinted Polymer on a Plasmonic Plastic Optical Fiber to detect perfluorinated compounds in water," Sensors, vol. 18, pp. 1836, 2018.

[27] N. Cennamo, G. D'Agostino, M. Pesavento, and L. Zeni, "High selectivity and sensitivity sensor based on MIP and SPR in tapered plastic optical fibers for the detection of L-nicotine," Sensors and Actuators B., Vol. 191, pp. 529–536, 2014.

[28] N. Cennamo, L. De Maria, G. D'Agostino, L. Zeni, and M. Pesavento, "Monitoring of Low Levels of Furfural in Power Transformer Oil with a Sensor System Based on a POF-MIP Platform," Sensors, vol. 15, pp. 8499-8511, 2015.

[29] K. Gasior, T. Martynkien, and W. Urbanczyk, "Effect of constructional parameters on the performance of a surface plasmon resonance sensor based on a multimode polymer optical fiber," Appl. Opt., vol. 53, pp. 8167-8174, 2014.

[30] K. Gasior, T. Martynkien, G. Wojcik, P. Mergo, and W. Urbanczyk, "D-shape polymer optical fibers for surface plasmon resonance sensing," Opto-Electronics Review, vol. 25, pp. 1–5, 2017.

[31] L. Uzun and A.P.F. Turner, "Molecularly-imprinted polymers sensors: realising their potential," Biosens. Bioelectron., vol. 76, pp. 131–144, 2016.

[32] K. Haupt and K. Mosbach, "Molecularly imprinted polymers and their use in biomimetic sensors," Chem. Rev., vol. 100, pp. 2495–2504, 2000.

[33] Y. Taguchi, E. Takano, and T. Takeuchi, "SPR Sensing of Bisphenol A Using Molecularly Imprinted Nanoparticles Immobilized on Slab Optical Waveguide with Consecutive Parallel Au and Ag Deposition Bands Coexistent with Bisphenol A-Immobilized Au Nanoparticles," Langmuir, vol. 28, pp. 7083−7088, 2012.

[34] B.I. Burganov, A.V. Lobanov, I.A. Borisov, and A.N. Reshetilov, "Criterion for Hill equation validity for description of biosensor calibration curves," Anal. Chim. Acta, vol. 427, pp. 11-19, 2001.