Molecularly Imprinted Polymers for VOC Sensing: chemoresistive and optical Sensors

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Abstract

Nowadays, Volatile Organic Compounds (VOC's) in indoor air are considered as a big pollution issue. VOC's originate from furniture, paintings, varnishes, wood protection, construction materials, etc. In particular, formaldehyde is one of the priority pollutants because of its carcinogenic character and its omnipresence in our close environment. Methods based on air sample collection and lab measurements are the most used measurement techniques today but although they are accurate and reliable, they are expensive, not real time and cause statistics issues. Devices based on chemical sensors are a good solution as these systems can be very sensitive, low cost, real time and easily integrated in common electronics to build portable systems. This paper presents formaldehyde sensors based on molecularly imprinted polymer (MIP).
MIP is a polymer synthesized incorporating a template molecule. Functional monomers form a complex around the template and are linked afterwards to form a polymer constituted of a series of "cages" trapping the template. Afterwards, the template is removed, leaving cavities imprinted in the polymer matrix that allows the polymer to selectively recognize the target molecule. These elements are cheap, easy to synthesize and can be adapted to any kind of surface. When using conducting polymers for building MIP's, the adsorption of the template can modify their optical or electrical properties. We showed that it was possible to use these materials for building chemoresistive or optical fiber sensors working at room temperature for detecting formaldehyde with a good selectivity and fair sensitivity.

Keywords
Polypyrrole, formaldehyde, sensor, Molecularly Imprinted Polymer.

Introduction

Volatile Organic Compounds in indoor air have become these last years the subject of a big concern. The main emission sources are: furniture, paintings, varnishes, wood protection, construction materials, etc. In particular, formaldehyde is now considered by the authorities as one of the priority pollutants because of its carcinogenic [1] character and because of the multiplication of sources in our close environment. The world health organization (WHO) guideline for indoor air formaldehyde concentration is 80 ppb (0.1 mg/m^3) [2]. Methods based on air sample collection and lab measurements are available and are the most used measurement techniques [3]. They are accurate and reliable but these methods are expensive, are not real time and cause statistics issues because of that. That is why, it is important to detect and measure formaldehyde in real time, in situ and with a low cost piece of equipment. Devices based on chemical sensors are good solutions as these systems can be very sensitive, low cost and easily integrated in common electronics to build portable systems [4]. Chemical gas sensors are based on the monitoring of the changes of the physical properties of a sensitive coating in contact with a target gas. Indeed, reversible adsorption of the gas can provoke a change in density (mass increase), permittivity, conductivity,color or refractive index (in some cases, several properties can be modified simultaneously). The pertinent physical property is then measured thanks to a transducing platform that converts the "chemical signal" to an electrical or optical signal that can be read by classical electronics. What ever the tranducing mechanism, the performance of the sensor are related to the performances of the sensing layer.

In this paper, we present two kinds of sensors that use the same sensitive material, a molecularly imprinted polymer, exploiting either the optical property variation or the electical conductivity change.

Molecularly imprinted polymers (MIP's) are polymers that are synthesized incorporating the target molecule we want to detect as a template. Functional monomers form a complex around the template and are linked afterwards to form a polymer constituted of a series of "cages" trapping the template. Once the synthesis is complete, the template molecule is extracted, leaving molecular cavities imprinted in the polymer matrix that allows the polymer to selectively recognize the target molecule [5, 6]. These elements are cheap, easy to synthesize and can be adapted to any kind of surface. Molecular Imprinting Technology (MIT) is a versatile and promising technology for practical applications in many areas, such as antibody receptors [7,8], protein separation [9-11], pollutant determination [12], catalysis [13, 14], drug delivery [15] and chemical sensors [16-19].

The refractive index of a MIP layer is different in the absence of the target than when it is present and MIP's can be good candidates as sensitive layers for optical sensors provided they are deposited on a transducing system able to monitor optical properties.

Several approaches have been developed to use MIP's on plastic optical fibers (POFs) [20, 21] or based on the removal of the fiber cladding in order to let the light in the core interact with the polymer coating [22, 23]. However, through the use of tilted fiber Bragg gratings (TFBGs) [24, 25], it is possible to obtain light interaction with an outer medium by using a single-mode silica optical fiber while avoiding the removal of its cladding. TFBGs are periodic modulations of the refractive index of the core of an optical fiber that are angled with respect to the perpendicular to the fiber longitudinal axis. The transmission spectrum of such a modified fiber presents a series of peaks that are sensitive to refractive index changes of the surrounding medium. The change of the peaks (amplitude or wavelength shift) are associated with the refractive index of the surrounding medium and, as such, a TFBG can be used as a refractometer. An optical sensor can be easily obtained by depositing a sensitive layer that changes its refractive index on the fiber. The adsorption of the target molecule will change the transmission spectrum and the change of the peaks (amplitude or wavelength shift) is in direct relation with the concentration. Moreover, it is possible to design TFBG sensors able to excite a surface plasmon polariton (SPP) [26, 27] by optimizing the grating characteristics and metallic coating thickness, what has been demonstrated to significantly increase their refractometric sensitivity. The surface plasmon resonance (SPR) technique has already been used for optical chemical sensing [28] but in the case of TFBG-SPR sensors, their scope has been limited to liquid environments, typically focused on biosensing applications [29]. Metallic thin films can be easily deposited around optical fibers, for example by sputtering, providing at the same time a suitable surface to synthesize conductive polymers by electropolymerization mechanisms. The advantage of using optical fiber is that it is possible to deposit several layers on the same fiber and monitor each grating allowing quasi-distributed measurements over long distances.

On the other hand, local measurements, resistive gas sensors are simple and cheap. Resisitive gas sensors or chemoresistors consist of a pair of interdigitated electrodes deposited on an insulating substrate and covered by a semiconducting sensitive layer.
Using conducting polymers for building MIP's allows to get resistive gas sensors working at room temperature with a good selectivity.
In this work, polypyrrole (PPy) was chosen as a sensitive coating,.It is a conductive polymer [30, 31] with the advantage of being easily synthesized and deposited by electropolymerization [32, 33]. Polypyrrole is obtained by the oxidation of pyrrole. This process allows a good control of the deposition and provides a good adhesion with the metal electrodes. In our case, the PPy is deposited on gold electrodes. Here gold is used for the interdigitated electrodes of the chemoresistor or for the SPR generation on the optical fiber.

Preparation of the MIP
The template molecule of the MIP was formaldehyde (CH_2O), the monomer precursor of the MIP was composed of a mixture of pyrrole and 15 wt% of pyrrole-3-carboxylic acid (figure 1), since the latter

binds with CH_2O through hydrogen bonds, creating a complex that is linked with pyrrole. Figure 1 shows a scheme of the MIP molecular structure of pyrrole-3-carboxylic acid and of the bond that is created during the polymer synthesis, respectively.

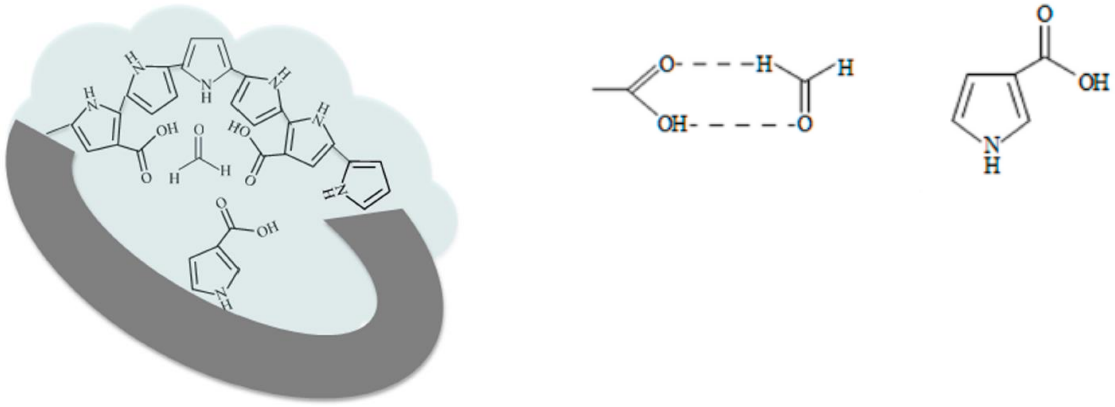


Fig. 1. Scheme of the MIP before extraction (left). Pyrrole-3-carboxylic acid and hydrogen bond with formaldehyde (right) .

The solution for the electropolymerization consists of 50 ml of acetonitrile (99.8% anhydrous), 0.62 g of sodium perchlorate, 0.335 ml of pyrrole, 0.07 g of pyrrole-3-carboxylic and 100 µl of formaldehyde solution (37 wt% in water). All reactants were purchased from Sigma-Aldrich. The electropolymerization setup is described in reference [19]. The cell consists in a gold layer which acts as anode, a stainless steel counter electrode as cathode, and an Ag/AgCl reference electrode. The electropolymerisation process consists in cycles from 0 to + 0.9 V. The thickness is controlled by the imposed number of cycles. After the electropolymerization, the sensor was rinsed with ethanol and put in a mixture of 1/3 acetic acid and 2/3 methanol for 8 hours to extract the template from the MIP.
For comparison, samples deposited in the same conditions but without formaldehyde, called NIP, were prepared.
Figure 2 shows a FE-SEM picture of a MIP film. All the films present a typical cauliflower structure.

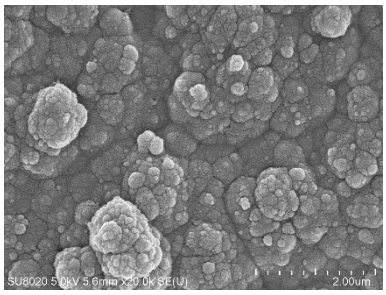
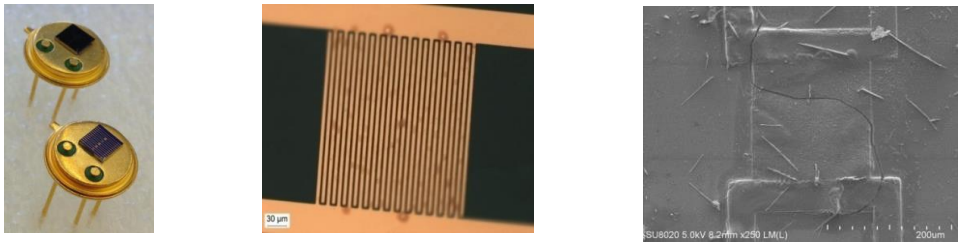


Fig.2. FE-SEM of the polypyrrole film.

Resistive sensor

The sensor consists in gold interdigitated electrodes deposited on a SiO_2/Si substrate (Figure 3A and B). The chips are bonded in a 2 pin-TO header (the third pin is grounded). The sensitive film was directly grown by electropolymerization on the electrodes according to the procedure described above. The electrode width and the finger spacing are 2 µm. A 5-µm-thick MIP film was deposited which can cover the metallic electrodes with a continuous film (Figure 3C). This method provides a good adhesion and the sensitive layer is deposited only on the useful area avoiding a further photolithography step.



A B C

Fig. 3. Pictures of the fabricated sensors: (A) General view; (B) Electrodes before deposition; (C) SEM picture of electrodes covered with MIP PPy film.

Gas tests

The sensors were placed in a Teflon gas cell and exposed to formaldehyde at various concentrations in humid air (50 % RH at 25°C) thanks to a set of mass flow controllers imposing a constant total flow of 1000 ml/min.

Figure 4 shows the response of a MIP to a 3 ppm formaldehyde injection in humid air (50 % RH @ 25°C). Both response and recovery times are fairly short. The t_{90} is about 5 min. Polypyrrole is a well known p-type semiconductor. The adsorption of formaldehyde, reducing gas and electron donor, provokes a decrease of the hole concentration and therefore an increase of the resistance. The adsorption of formaldehyde is reversible.

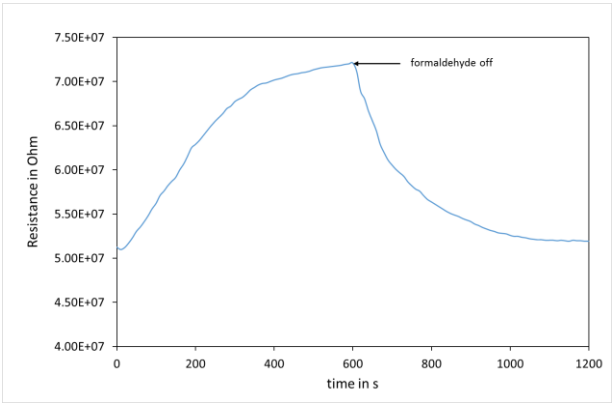
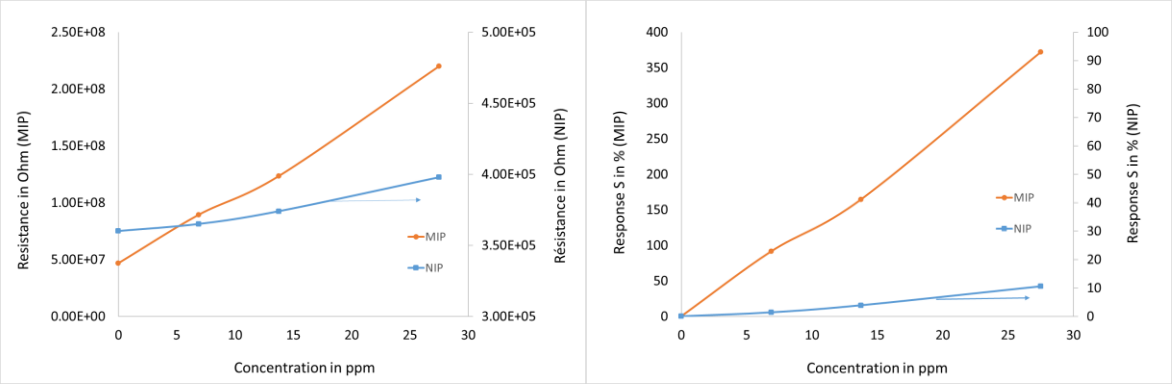


Fig. 4. Resistance of MIP and NIP sensors to formaldehyde injections in moist air (RH=50 % at 22°C).

Figure 5 shows the response versus formaldehyde concentration of a MIP and the corresponding NIP at equilibrium. The response S is defined as the ratio $(R_{gas}-R_{air})/R_{air}$ in %. The NIP shows a small response while the MIP shows a rapid reponse proving the MIP effect.



A B

Fig. 5. A Resistance of the sensors (MIP and NIP) and B response versus formaldehyde concentration.

Tests were also performed with 20 ppm of methanol, ethanol and acetone. No response was visible, indicating that the sensor has a good selectivity.

Optical fiber sensor

A 50 nm-thick film of MIP is deposited on top of a gold coated fiber provided with a TFBG (tilt angle = 6°, length= 1 cm). Gold is used as an electrode for the electrodeposition following the same process as explained above. The TFBG was previously photo-inscribed in the core of a single-mode photosensitive optical fiber (FiberCore PS-1250). The photoinscription consists in exposing the fiber to a 244 nm UV beam from a frequency-doubled continuous wave (CW) Ar laser focalized on a 1095.08 nm pitch phase-mask previously tilted to obtain the desired angle at the grating planes. The fiber was hydrogen loaded before the grating inscription in order to increase its photosensitivity. After the inscription, the grating is annealed at 85°C for 24 hours to remove the hydrogen. The gold layer with 20 nm thickness is deposited on the fiber by sputtering in a Leica EM SCD 500 metallizer. Figure 6 shows a cross section of the stacking.

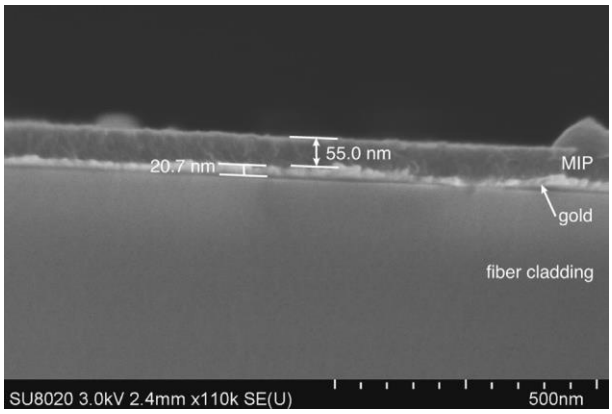


Fig. 6. SEM image of the layers on the silica optical fiber (cross section).

The optical fiber sensor is placed in a glass chamber for the exposure to gases. The chamber is flown with humid air (50 % RH at 22°C) with a total flowrate of 1000 ml/min. The transmission spectrum of the fiber is monitored with an optical vectorial analyzer (OVA) from Luna Technologies. A polarizer was used to select both the radial and azimuthal polarizations.

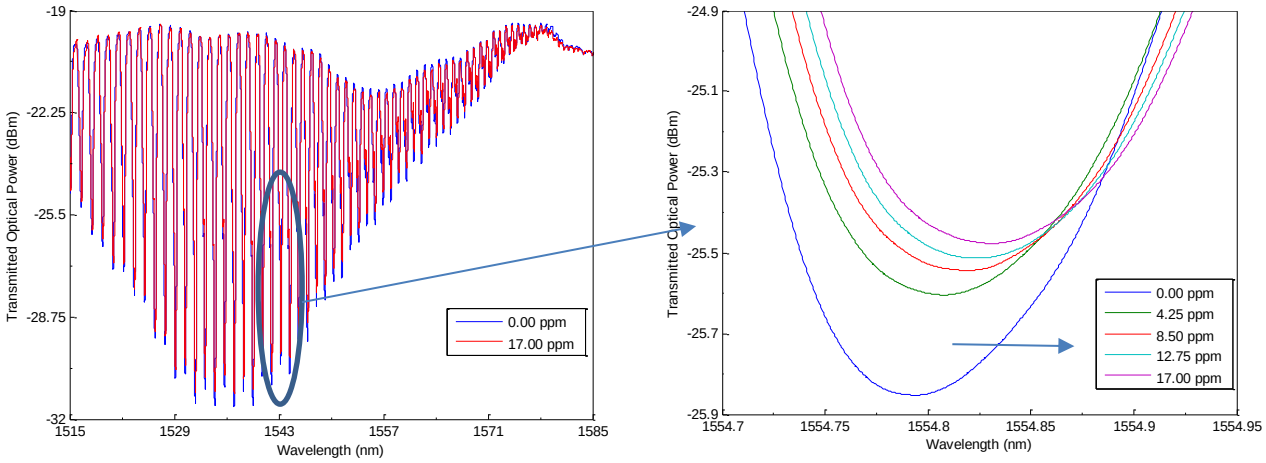


Fig. 7. Transmitted spectrum measured during the test for several concentrations (A), zoom of one of theresonances (B).

Figure 7A shows the global transmission spectrum. A zoom on a selected wavelength is presented in figure 7B.

The wavelength shift is due to the increase of the refractive index as the pores are filled by the target gas.

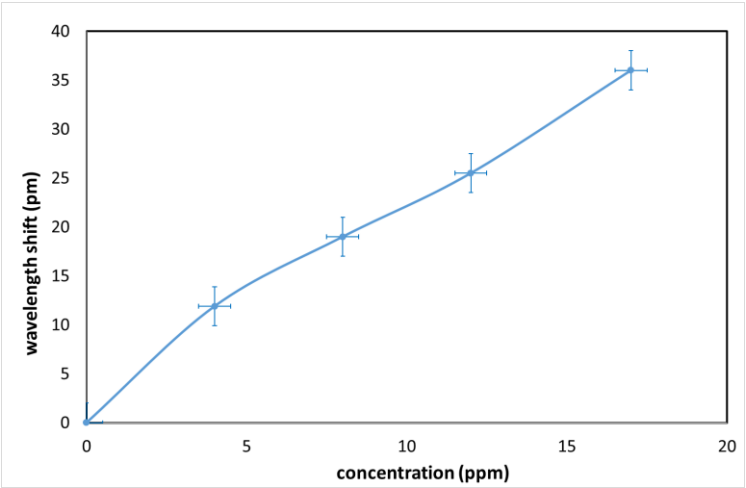


Fig. 8. Wavelength shift (around 1545 nm) versus concentration for formaldehyde.

Injections of CH_2O lead to a red shift of the peaks corresponding to an increase of the refractive index of the MIP layer. Figure 8 shows the wavelength shift in nm versus concentration for CH_2O.
Similar tests were performed with acetone, ethanol and toluene to check the selectivity. The results are summarized in Table 1.

	formaldehyde	ethanol	acetone	toluene
shift (pm)	25.5	5.3	4.5	3.3

Table 1. Wavelength shift at 1555 nm for 12 ppm CH_2O injections.

The sensitivity for formaldehyde largely exceeds the other tested gases showing the selectivity of the sensor towards these potential interfering gases.
Notice that, like with resistive sensors, exposure of the fibers covered with the corresponding NIP films led to an insignificant response for all gases.

Conclusions

This paper presents the use of a Molecularly Imprinted Polymer as a recognition layer for the detection of formaldehyde. When using conducting polymers for building MIP's, the adsorption of the template can modify their optical or electrical properties. Our results show that it was possible to use these materials for building chemoresistive or optical fiber sensors for formaldehyde working at room temperature with a good selectivity. The present sensitivity does not allow their use for the monitoring of low concentrations in the ppb range but are suitable for the ppm range.

References

1. World Health Organization IARC (2006) Formaldehyde, 2-Butoxyethanol and 1-tert-Butoxypropan-2-ol. IARC monographs on the evaluation of carcinogenic risks to humans, Lyon, 88:39-325.
2. World Health Organization, Regional Office for Europe (2010) WHO guidelines for indoor air quality: selected pollutants, Geneva, ISBN: 9789289002134.
3. Vairavamurthy A, Roberts JM, Newman L (1992) Methods for determination of low molecular weight compounds in the atmosphere: a review. Atmos. Environ. 26A:1965-1993.
4. Chung P R, Tzeng C T, Ke M T and Lee C Y (2013) Formaldehyde Gas Sensors: A Review. Sensors 13: 4468-4484.
5. Haupt K, Linares A V, Bompart M, Bui B T (2011) Molecularly Imprinted Polymers, K. Haupt, Ed., Springer Berlin Heidelberg, 1–28.
6. Vasapollo G, Del Sole R, Mergola L, Lazzoi M R et al (2011) Molecularly Imprinted Polymers: Present and Future Prospective. International Journal of Molecular Sciences 12:5908–45.
7. Longo L and Vasapollo G (2008) Pc-Based Molecularly Imprinted Polymers as Nucleoside Receptors. Metal-Based Drugs:1–5.
8. Whitcombe M J, Kirsch N and Nicholls I. A (2014) Molecular Imprinting Science and Technology: A Survey of the Literature for the Years 2004-2011. Journal of Molecular Recognition 27:297-401.
9. Shiomi T, Matsui M, Mizukami F and Sakaguchi K (2005) A Method for the Molecular Imprinting of Hemoglobin on Silica Surfaces Using Silanes. Biomaterials 26:5564–71.
10. Bossi A, Bonini F, Turner A P F and. Piletsky S A (2007) Molecularly Imprinted Polymers for the Recognition of Proteins: The State of the Art. Biosensors and Bioelectronics 22:1131–3.

11. Rossetti C, Qader A A, Grønhaug Halvorsen T, Sellergren B and Reubsaet L (2014) Antibody-Free Biomarker Determination: Exploring Molecularly Imprinted Polymers for Pro-Gastrin Releasing Peptide, Analytical Chemistry 86:12291–98.
12. Pichon V and Chapuis-Hugon F (2008) Role of Molecularly Imprinted Polymers for Selective Determination of Environmental pollutants—A Review. Analytica Chimica Acta 622:48–61.
13. Katz A, Davis M E (2000) Molecular imprinting of bulk, microporous silica. Nature 403, 20:283-289.
14. Li W and Li S (2006) Molecular Imprinting: A Versatile Tool for Separation, Sensors and Catalysis Oligomers and Polymer Composites Molecular Imprinting. Springer Berlin Heidelberg 206:191–210.
15. Piletsky S, Turner N W and Laitenberger P (2006) Molecularly Imprinted Polymers in Clinical diagnostics—Future Potential and Existing Problems. Medical Engineering & Physics 28:971–77.
16. Dickert F L and Hayden O (1999) Molecular Imprinting in Chemical Sensing, TrAC Trends in Analytical Chemistry 18:192–199.
17. Blanco-Lopez M C, Gutierrez-Fernandez S et al (2004) Electrochemical Sensing with Electrodes Modified with Molecularly Imprinted Polymer Films. Analytical and Bioanalytical Chemistry 378:1922–28.
18. Chen W, Ma Y, Pan J et al (2015) Molecularly Imprinted Polymers with Stimuli-Responsive Affinity: Progress and Perspectives. Polymers 7:1689–1715.
19. González-Vila Á, Debliquy M, Lahem D, Mégret P and Caucheteur C (2017) Formaldehyde sensing with plasmonic near-infrared optical fiber. Sensors and Actuators B 244:1145–1151.
20. Cennamo N, D'Agostino G, Pesavento M and Zeni L (2014) 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 191:529–536.
21. Cennamo N, De Maria L, D'Agostino G, Zeni L and Pesavento M (2015) Monitoring of low levels of furfural in power transformer oil with a sensor system based on a POF-MIP platform. Sensors 15:8499–8511.
22. Zamarre˜no C R, Hernáez M, Del Villar I, Matías I R and Arregui F J (2011) Optical fiber pH sensor based on lossy-mode resonances by means of thin polymericcoatings, Sensors and Actuators B 155:290–297.
23. Agrawal H, Shrivastav A M and Gupta B D (2016) Surface plasmon resonance based optical fiber sensor for atrazine detection using molecular imprinting technique. Sensors and Actuators B 227:204–211.
24. Albert J, Shao L Y and Caucheteur C (2013) Tilted fiber Bragg grating sensors, Laser Photon Rev 7:83–108.
25. Guo T, Liu F, Guan BO and Albert J (2016) Tilted fiber grating mechanical and biochemical sensors. Opt Laser Technol 78:19–33.
26. Shevchenko Y Y and Albert J (2007) Plasmon resonances in gold-coated tilted fiber Bragg gratings. Opt Lett 32:211–213.
27. Caucheteur C, Voisin V and Albert J (2013) Polarized spectral combs probe optical fiber surface plasmons. Opt Express 21:3055-3066.
28. Paliwal A, Sharma A, Tomar M and Gupta V (2015) Room temperature detection of NO2 gas using optical sensor based on surface plasmon resonance technique, Sensors and Actuators B 216:497–503.
29. Caucheteur C, Guo T and Albert J (2015) Review of plasmonic fiber optic biochemical sensors: improving the limit of detection. Anal Bioanal Chem 407:3883–3897.
30. Ates M (2013) A review study of (bio)sensor systems based on conducting polymers, Mater Sci Eng C 33:1853–1859.
31. Byshkin M S, Buonocore F et al (2015) A unified bottom up multiscale strategy to model gas sensors based on conductive polymers, Sensors and Actuators B 211:42–51.
32. Zhou M and Heinze J (1999) Electropolymerization of pyrrole and electrochemical study of polypyrrole: Evidence for structural diversity of polypyrrole. Electrochim Acta 44:1733–1748.
33. Petitjean J, Aeiyach S, Lacroix J and Lacaze P (1999) Ultra-fast electropolymerization of pyrrole in aqueous media on oxidizable metals in a one-step process, J Electroanal Chem 478:92–100.