

Volatile Organic Compounds Fibre Optic Nanosensor

César Elosúa^a, Cándido Bariáin^a, **Ignacio R. Matías^a**, Francisco J. Arregui^a, Asunción Luquin^b,
Mariano Laguna^c, Julián Garrido^b

^aDepartamento de Ingeniería Eléctrica y Electrónica, Universidad Pública de Navarra, Campus de Arrosadia s/n, 31006 Pamplona, Spain

^bDepartamento de Química Aplicada, Universidad Pública de Navarra, 31006 Pamplona, Spain

^cInstituto de Ciencia de Materiales de Aragón-CSIC, Universidad de Zaragoza, 50009 Zaragoza, Spain
natxo@unavarra.es

Abstract

A novel vapochromic material of formula $[\text{Au}_2\text{Ag}_2(\text{C}_6\text{F}_5)_4(\text{C}_6\text{H}_5\text{N})_2]$ has been used to develop a volatile organic compounds (VOCs) sensor. This product changes its optical properties, such as colour or refractive index, when exposed to some organic vapours. The sensor consists of a nanometer-scale Fizeau interferometer doped with the above mentioned vapochromic complex and built onto a cleaved end of a multimode fibre optic pigtail by using the Electrostatic Self Assembly Method (ESA). The fibre optic sensor is used in a reflection scheme, so the other extreme of the optical fibre pigtail is connected to an optical coupler, completing the set up with an optical source that generates an interrogating signal and an optical detector to collect the intensity modulated reflected optical power. Absorbance spectra and the response of the sensor for different VOCs concentration at a certain wavelength (850 nm) were studied. Changes up to 3 dB in the reflected optical power were registered.

Keywords: fibre optic sensor; gas sensor; vapochromic material; ionic self-assembly monolayer, nanocavities, nanodeposition, thin films.

1 Introduction

Detection of VOCs is a very important aim in sensing technology. In the last few years many researching groups have been focusing their attention in this type of sensors towards environmental applications, electronic noses, food or chemical industry, just to mention a few. Most of these sensors consist of polymer-based electronic devices.

Fibre optic sensors offer some advantages that make them a good alternative to electronic ones, showing a passive nature, immunity to electromagnetic noise, small size and light weight avoidance of ground loops, durability, remote operation or capability of multiplexing among other advantages. Most fibre optic optical sensors are based on the modulation of the light intensity produced by the substance to be detected [1,2], which provokes a change on one of the optical properties of the sensing material, such as absorption or refractive index.

In this work, a new vapochromic complex, whose optical properties change in presence of volatile compounds, acts as the sensing material. Following the ESA method, ionic monolayers doped with this complex are deposited on the cleaved end of a fibre optic pigtail in order to develop a nano-cavity sensitive to volatile organic compounds vapors.

2 Vapochromic material

For the preparation of a suitable detector of VOCs, it is necessary to find a complex able to change some properties in presence of such a VOC. A change in colour or in refractive index is easy to detect with a simple scheme consisting of a light source and an optical fibre device. In our case, we found new gold complexes that show this commented behaviour known as vapochromism in solid state.

There is a family of complexes of general formula $[\text{AuAg}(\text{C}_6\text{F}_5)_2\text{L}]_n$, where L can be pyridine, 2,2'-bipyridine, 1,10 phenantroline, 1/2 diphenylacetylene and other ligands [3,4], which change from different colour as orange or red to white in the presence of coordinating solvent as methanol or ethanol. Some fibre optic sensor based on this family of complexes was presented and characterized for VOCs detection [5]. In this work, a gold-silver complex based on pyridine has been employed. This product is presented in form of bright red powders.

3 Experimental set-up

3.1 Optical fibre pigtail

The multimode optical fibre chosen for this purpose has a core and cladding diameters of 62,5 μm and 125

μm , respectively, and the end of which is cut with a Siemens S46999-M9-A8 precision fibre cleaver. The small size of the sensor head carries enormous advantages. Among them, one can mention its low cross-correlation to temperature, robustness, reproducibility, fast response, possibility of using optical sources with low coherent length, etc. Furthermore, it makes possible to use an interrogating/detection scheme similar to the used in intensity based sensors, although the sensor has an interferometric nature, as will be demonstrated later.

The experimental reflection set-up employed is shown in figure 1. A Y coupler 50:50 was used to connect the system. This device has also a $62.5 \mu\text{m}$ core diameter, which avoids insertion losses.

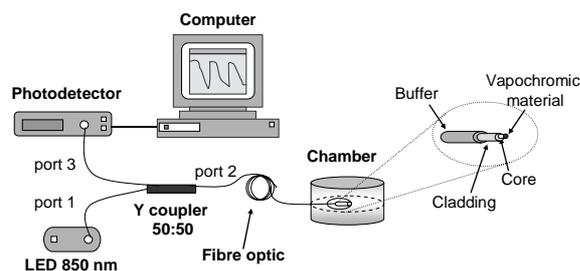


Figure 1: Set-up implemented to analyze the response of the fibre optic based sensor.

The sensor head is connected to port 2 and the other two ports are connected to the 850 nm LED source (port 1) and to the photodetector, 675RE from RIFOCS Corporation (port 3). When measuring the reflected optical power during the Fizeau nanocavity construction process, the fibre end is stayed on air. In order to study the response of the sensor when exposed to VOCs, the sensor head is introduced into a chamber closed hermetically (diameter: 9 cm, high: 2 cm, volume: 275 cm^3), where different VOCs are introduced in liquid phase.

4 Nanosensor implementation

4.1 Electrostatic Self-Assembly Method

The ESA method is a technique already proven for the deposition of several materials [6]. In last few years, it has been presented as a very useful technique to build up two-beams Fabry-Perot (also called Fizeau) nanocavities on optical fibre with lengths less than a micrometer [7]. Simplicity or reproducibility are the main advantages this method presents respect to other deposition techniques employed to develop optical fibre sensors such as sol-gel [8,9], dip coating [10] or Langmuir-Blodgett [11].

The ESA process involves several steps. Firstly, a substrate (in this case optical fibre), is cleaned and chemically treated to produce a charged surface. Then the substrate is alternately dipped into solutions of cationic and anionic polymers to create a multilayer

thin film. The individual layer thickness or roughness can be controlled by adjusting some dipping parameters. The basic synthesis process is shown in figure 2.

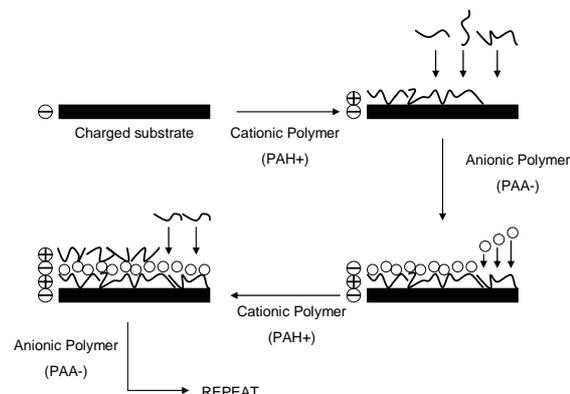


Figure 2: Schematic of the ESAM deposition process. The symbols are idealized and not intended to represent exactly the conformation of the polyelectrolyte chains.

In our work, a solution of PAH (poly allyamine hydrochloride) was used as the polycation, and PAA (poly acrylic acid) as the anionic polymer. The final multilayer structure built up at the end of an optical fibre, behaves as a homogeneous optical medium, because each monolayer thickness is on the nanometer scale, in the same scale than the wavelength of the source used. The layer thicknesses obtained are below the coherent lengths of LED, so they can be employed as optical sources instead of LASERS, reducing the cost of the final sensor system.

As above commented, the layer structure of the coating forms a two-beams interferometer nanocavity on the optical wavelength scale [12]. With the set up shown in figure 1, the evolution of the nanocavity can be registered, just monitoring the reflected optical power each time that a monolayer get deposited onto the end of the optical fibre. These measures will give a response similar to a Fizeau interferometer.

4.2 Doping the coating

The multilayer film structure had to be doped with the vapo-chromic material in order to obtain a VOC sensitive layer. First, it is necessary to decide in which polymer the vapo-chromic material has to be dissolved. PAH has an amine group that can give electrons to silver atoms of the vapo-chromic complex, acting as ligand (the same role than pyridine). The polycation is presented in hydrochloride form, so it has an acid behaviour. To avoid the vapo-chromic molecule destruction, the pH is raised to 7 in the PAH solution. The pH of the polyanion solution is also set at 7, in order to avoid problems in the construction of the structure [13].

Another additional problem is that the vapo-chromic material is not soluble in water but in organic

solvents. Some authors dissolved hydrophobic complex in an organic water-soluble solvent, yielding to a hydrophilic mixture [14]. In this case, we dissolved the vapochromic material in ethanol, and then some amount of water is added. Thus, the material can be incorporated into the polycationic solution.

The polyelectrolyte solutions volumes used were 10 mM, and the proportion between the vapochromic complex and ethanol was 1 mg per ml. 600 μ l of this solution were added to 20 ml of water, mixing this last solution with the cationic polymer, yielding to the final polycation solution.

4.3 Nano cavity construction

As commented above, a multilayer structure of form $[\text{PAH}^+(\text{Vap})/\text{PAA}^-]_n$, where n indicates the total number of bilayers, was built up at the cleaved end pigtail optical fibre. A total of 25 bilayers were deposited, curing the sensor for 1 hour at 50°C in order to eliminate ethanol rests that could remain at the surface after the deposition.

The experimental results obtained during the build up of the multilayer structure process are shown in figure 3. The curves represent the relative optical power for each polymer monolayer. The interferometric phenomenon has been monitored, so a nanocavity has been constructed at the end of the fibre. There are no differences bigger than 0.05 dB between each layer, so the structure has an adequate uniformity.

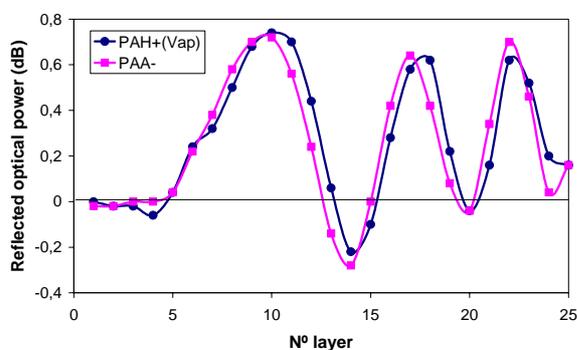


Figure 3: Construction curve of the sensor for the polycation (PAH⁺/Vap) and polyanion (PAA⁻).

5 Results and discussion

5.1 VOC assembly analysis

The first step in the measuring process is the introduction of the organic solvent into the chamber where the sensor head is located. After several minutes, the VOC gets vaporized, and the atmosphere inside the chamber becomes saturated starting the adsorption process at the nanocavity surface, changing its optical properties, and so, the reflected optical power collected. Once the reflected optical power is stabilized, the chamber is opened and the

optical power recovers its original value. This cycle has been done twice for ethanol (86 mmol/l) and methanol (125mmol/l), showing that the response is repetitive for each one, and that it can be used to discriminate between them. These results can be seen in figure 4.

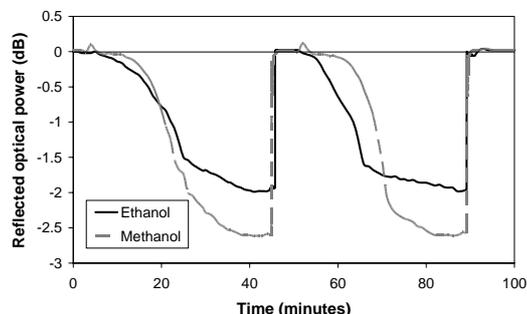


Figure 4: Comparison between the response of the sensor for ethanol and methanol.

In both cases, time response is around 30 minutes, which is longer than results reported in other VOCs sensors [15]. This is due to several factors as the curing applied to the sensor head, the doping process, the complex reaction time, but mainly to the time that the VOC takes to become a vapour inside the chamber. This last effect can be inferred from figures 4 and 5 by seeing the almost instantaneous recovery time of the sensor response once the chamber is open. Anyway, the influence of each one of these factors in time response is being studied and will be shown elsewhere in further works.

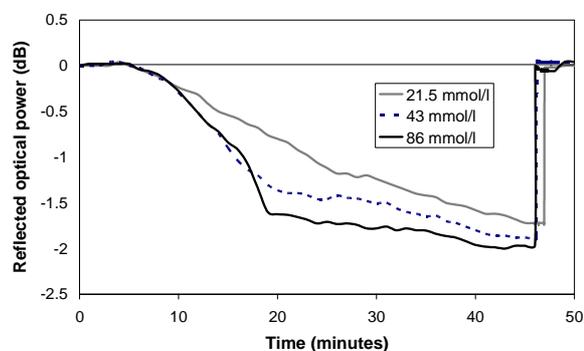


Figure 5: Response of the sensor for different ethanol concentrations.

5.2 VOC individual analysis

It has been studied the behaviour of the fibre optic sensor for different concentrations of ethanol: 21.5 mmol/l, 43 mmol/l and 86 mmol/l. The response of the sensor is shown in figure 5. From that figure, one can observe that the optical reflected power minimum level does not differ much between them, only 0.3 dB, being its time response the main difference between each measure: as the concentration decreases, the optical reflected power begins to fall later, and needs more time to get stabilized. This gives at least three possibilities to distinguish among concentrations: the

first one could be to measure the optical reflected power at a certain time since the ethanol is introduced into the chamber; another way is registering the time that the sensors takes to get its lower level, and finally, the fall slope can be used to discriminate between concentrations.

Finally, it is remarkable the fact that the sensor has been used inside the laboratory for at least one month, and no degradation in the doped nanocavity and neither variation in its behaviour has been observed.

6 Conclusions

An optical VOCs sensor has been experimentally developed. This device is based on a new vapochromic material which can detect some VOCs and determinate their concentrations. The technique employed to fabricate it is ESAM, which offers a high reproducibility and a very efficient use of the vapochromic complex, opening the way to further investigations to improve it. Using a cleaved end multimode pigtail fibre, the fabrication process takes only one day. Changes up to 3 dB in the reflected optical power have been registered.

7 Acknowledgements

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