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Volatile alcoholic compounds fibre optic nanosensor

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Abstract

A fibre optic sensor for detection of some volatile organic compounds (VOCs) is presented. This device is based on a new vapochromic material of formula $[Au_2Ag_2(C_6F_5)_4(C_6H_5N)_2]$, presented in the form of bright red powders. This material changes its optical properties as colour or refractive index when exposed to some organic vapours, recovering its original state when vapours get disappeared. The sensor head consists of a nanometer-scale Fizeau interferometer doped with the vapochromic material, 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 register the intensity modulated reflected measure. The response of the sensor has been characterized taking measures of its absorbance spectra and the intensity modulated reflected signal at 850 nm for different alcohols. Changes up to 3 dB in the reflected optical power were registered.
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1. Introduction

Detection of VOCs is a very important aim in sensor 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 [1]. They can help to determinate if the ripen process of a fruit is completed [2], or if the concentration in air of a chemical product excesses safety levels. Most of these sensors consist of polymer-based electronic devices. The amount of the VOC in the ambient and its reactivity with the polymer determine the response of the sensor. For example, researchers have used resistive sensors [3] to measure swelling of the polymer; capacitive sensors [4,5] to measure changes in polymer permeability, just to mention a few.

Fibre optic sensors are a good alternative to electronic ones: some of these electronic sensors need to be heated at 400 °C to detect VOCs [6], and at least all of them need to be biased to operate. Furthermore, an electric signal is required to get the sensor head biased/modulated, so they are not recommended in some explosive environments as chemical plants. Besides this, in presence of electromagnetic interferences, those electronic sensors do not operate properly. In order to solve these problems, optical fibre sensors shows 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 of the fibre optic sensors are based on the modulation of the light intensity produced by the substance to be detected [7]. The sensing element can be either the fibre itself or an external component fixed to the fibre. In any case, one of the optical properties, such as the colour, the refractive index or fluorescence, should get modified depending on the monitored substance in the surrounding environment.

In this work, a novel vapochromic complex, whose optical properties change in presence of volatile compounds, is used 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 giving rise to a nanocavity sensitive to alcoholic vapours.

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2. Vapochromic material

2.1. Materials

Organometallic chemistry is a new discipline that has been growing in interest in last few decades. Organic compounds are based on the ability of carbon to form bounds with other carbon atoms. Organometallic chemistry study this property in transition metal elements such us gold, silver or palladium, developing complexes with interesting applications [8].

For the preparation of a suitable VOC detector, it is necessary to find a complex whose properties change in presence of such a VOC. A change in colour or in refractive index is easy to detect with simple scheme consisting of a light source and an optical fibre-based device. Although there are a great number of complexes showing solvatochromism (change in absorbance properties when dissolved in different liquids), for the construction of VOCs sensors, it is more important another property as the vapochromism. This term was present firstly by Nagel [9] and Mann and co-workers [10] to describe complexes whose colour changes in presence of VOCs.

There is a family of complexes of general formula $[AuAg(C_6F_5)_2L]_n$, where L can be pyridine; 2,2′-bipridine; 1,10-phenantroline; 1/2-diphenylacetylene and other ligands [11,12], which change from different colour as orange or red to white in the presence of coordinating solvent as acetone, methanol or ethanol. In these cases the polynuclear structure of starting compound $[Au_2Ag_2(C_6F_5)_4(C_6H_5N)_2]$ disappears and a new anion–cation derivate was formed as a consequence of the solvent coordination to the silver centre and creaking both the gold–silver bounds and the gold–gold contacts, responsible of the initial colour. On the contrary the final cation–anion structure shows white colour (see Fig. 1). Some fibre optic sensor based on this family of complex were presented and characterized for VOCs detection [13].

Although it is quite necessary for a big quantity of solvent to provoke this effect completely, small quantities of solvent in vapour phase produce a detectable change in its refractive index.

In this work, the gold–silver complex based on pyridine has been employed for the detection of some VOCs. This product is present in form of bright red powders, and shows fluorescence at 575 nm.

3. Experimental set-up

The multimode optical fibre chosen for this purpose has a core and cladding diameters of 62.5 and 125 μm, respectively.

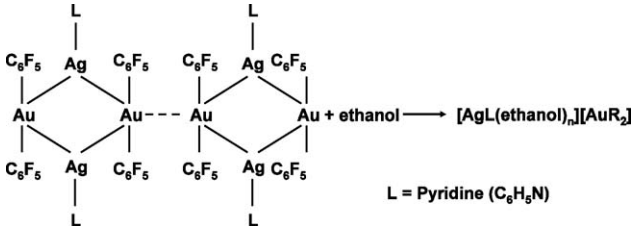

Fig. 1. Molecular structure of the new developed vapochromic material and its reaction in presence of ethanol vapours.

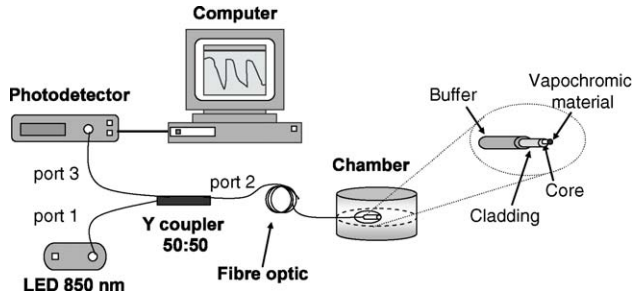

Fig. 2. Set-up implemented to analyze the response of the fibre optic-based sensor.

A 2 m pigtail of this fibre is cut at one end with a Siemens S46999-M9-A8 precision fibre cleaver. Finally, on this cleaver end the vapochromic material is deposited yielding to a nanocavity of several hundred of nanometres length. The small size of the sensor head implies enormous advantages. Among then, 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 make 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 Fig. 2. A Y coupler 50:50 was used to connect the system. This device has also a 62.5 μm core diameter, which avoids insertion loses.

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 deposition of several materials [14]. 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 [15]. Simplicity or reproducibility are the main advantages this method offers respect to other deposition techniques employed to develop optical fibre sensors such as for example sol–gel [16,17], dip coating [18] or Langmuir–Blodgett [19].

The ESA process involves several steps. Firstly, a substrate (in this case optical fibre), is cleaned and chemically treated with a mixture of sulphuric acid and hydrogen peroxide (3:1) 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 composition of each layer and the chemical

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