Sensors and Actuators B 202 (2014) 123–128

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Detection of hydrocarbons using suspended core microstructured optical fiber

T. Martan *, J. Aubrecht [1], O. Podrazký [1], Vl. Matějec [1], I. Kašík [1]

Institute of Photonics and Electronics ASCR, v.v.i., Chaberska 57, Prague 8, 182 51, Czech Republic

ARTICLE INFO

Article history:
Received 6 January 2014
Received in revised form 25 April 2014
Accepted 29 April 2014
Available online 24 May 2014

Keywords:
Microstructured optical fiber
Suspended core structure
Evanescent wave
Refractive index
Toluene vapors
Detection

ABSTRACT

Monitoring of dangerous hydrocarbons is an important issue for both chemical process control in industry and protection of the environment. Vapors of toluene are highly dangerous in low concentrations because of its low explosive limit of 1.2 mol%. Toluene vapors in concentrations lower than the explosive limit can be detected using a fiber optic arrangement containing a short section of suspended core microstructured optical fiber (SC MOF). We prepared the SC MOF for this purpose, with an inner structure consisting of a relatively thin silica core, 2.6 μm in diameter, surrounded by three large cladding holes with radii of 26 μm, which were designed to be large enough for trouble-free analyte flow. It has been shown that a 0.3 m-long SC MOF sensing element can be used for refractometric detection of toluene vapors in low concentrations without using any other adsorption layers. We have experimentally verified the operational reversibility of the SC MOF sensing element in time. A sensitivity of 1.20 ± 0.04 dB/mol% and a detection limit of 0.0079 mol% have been determined for this sensing element. The SC MOF can detect sufficiently low concentrations of toluene vapors to reveal safety risks before the toluene reaches the lower explosive limit.

1. Introduction

Continuous monitoring of dangerous and explosive hydrocarbons (HCs) is an important issue for the protection of human health and the environment and for the control of chemical processes in industry [1]. Conventional sensors based on semiconductors [2], surface acoustic waves [3] or a quartz crystal microbalance combined with polymers [4,5] were designed and tested for the detection of gaseous HCs in air or liquid HCs dissolved in water. Unfortunately, all these detection principles use electrical quantities, and are unsuitable for long term monitoring of concentrations of HCs due to dangerously low explosive limits of HCs (e.g. [31]) combined with electrical detection tools.

Sensors based on silica optical fibers in different detection arrangements, e.g. remote (distributed) detection [6,7], seem to be more suitable for flammable or explosive HC detection since their detection principle is based on light propagation and thus eliminate the risk of sparking. Moreover, they are not flammable, are resistant to high temperatures, are insensitive to electromagnetic interference. For the purposes of remote HC detection [8], various fiber optic tools were used, such as telecommunications fibers with Bragg gratings [9,10], and inverted graded index (IGI) fibers [11] or polymer clad silica (PCS) fibers [12–14] combined with coated adsorption layers for enhanced sensitivity [15–19].

One special group of fibers intended for detection applications are microstructured optical fibers (MOFs) [20–27]. The type of MOF chosen for use in this paper, the suspended core microstructured optical fiber (SC MOF), represents a promising way to detect gaseous analytes that flow through the fiber cladding [28–30].

The measured gases flow under pressure (e.g. inside a pipeline), and part of this gas is guided to the cladding holes of the SC MOF via a pressure coupling element. Toluene (vapors of toluene) was chosen from a family of hydrocarbons (arenes) for experimental testing of the designed SC MOF because vapors of toluene are highly flammable and explosive [31]. The detection method was based on a refractometric principle, using the evanescent wave propagating along the core–cladding boundaries of the SC MOF. When using this method for concentration measurement, the composition of the tested gaseous analyte is assumed to be known in terms of its refractive index because this method is not selective. The refractive index of tested gas should be lower than the refractive index of fused silica (a material of the fiber core) at the measured wavelength.

The paper focuses on pure silica SC MOFs without any detection (sorption) layers, which were prepared and used for toluene vapors detection.

* Corresponding author. Tel.: +420 220 922 391; fax: +420 284 680 222.
E-mail addresses: martan@ufe.cz (T. Martan), aubrechtj@ufe.cz (J. Aubrecht), podrazky@ufe.cz (O. Podrazký), matejec@ufe.cz (Vl. Matějec), kasik@ufe.cz (I. Kašík).
[1] Tel.: +420 220 922 391; fax: +420 284 680 222.

http://dx.doi.org/10.1016/j.snb.2014.04.103
0925-4005/

2. Experimental

2.1. Principle of detection

The refractometric principle of detection was based on the overlap of the evanescent wave propagating along the core–cladding boundaries with gaseous analyte (toluene vapors in nitrogen) propagating in the cladding holes of the SC MOF. The evanescent wave(s) of mode(s) guided in the fiber core interacts with toluene vapors of different concentrations that cause slight changes in the refractive index of the cladding structure. This effect induces changes in the output power of the light guided in the SC MOF core. The F-D F-D package in COMSOL 3.5 (Cosmol Multiphysics) program was employed for numerical analysis of the SC MOF inner structure.

The designed SC MOF characteristically has a small diameter silica core and large cladding air holes, as shown in Fig. 1(a). Longitudinal section of the SC MOF showing the evanescent wave is shown in Fig. 1(b).

2.2. Fabrication and characterization of the SC MOF

The designed SC MOF was drawn from a preform prepared by a "stack and draw" method. An all-silica preform was assembled from a cladding tube and three capillaries. Capillaries with outer and inner diameters of 1.8 mm and 1.4 mm, respectively, and a tube with outer and inner diameters of 12 mm and 4 mm, respectively, were used. The preform was placed in a graphite furnace, pressurized at about 6 kPa and drawn into a fiber at a temperature of 1970 °C.

The SC MOF was fabricated with a core diameter of 2.66 μm and a silica bridge thickness of 0.9 μm. The cladding holes of the SC MOF each had a radius of 26 μm. The SC MOF was drawn with an overall diameter of 125 μm. A micro-photograph of the cross-section of the SC MOF produced by an optical microscope Olympus BX-51 is shown in Fig. 2(a), and a detailed image of the core area of the SC MOF with the silica bridges produced by a scanning electron microscope (SEM) Jeol JSM-6510 is shown in Fig. 2(b).

The prepared SC MOF was then characterized. The spectral attenuation of the SC MOF in a wavelength range from 1400 nm to 1650 nm was measured by a cut-back method (without the analyte in the cladding holes) by using an AQ-6315A optical spectral analyzer and a Safibra OFLS 6 – dual optical fiber-coupled superluminescent light-emitting diode (SLED) source. We applied the SLED source and a USB 2000 spectrometer (PC controlled) to detect the different concentrations of toluene vapors.

2.3. Toluene vapors detection using the SC MOF

A commercially available 1450–1750 nm wideband SLED source for a band of wavelengths around 1550 nm and a 30 cm-long SC MOF element connected to standard single-mode optical fiber (SMF) patchcords via pressure coupling elements (PCEs) with gas input and gas output pipes were used. The USB 2000 spectrometer and a PC were used to evaluate the output power dependence on the gas mixture composition. The curves were measured in absolute values. The attenuation in dB was calculated by using the formula $10\log(P_0/P)$, where P_0 is a reference (the output power for pure nitrogen) and P is the output power measured for a particular toluene mixture (vapors of toluene and nitrogen). The flow of the toluene mixture was measured at the end face of the SC MOF by using a gas flow controller that was connected to the gas output pipe. The entire measurement setup was sealed to conserve the internal pressure of the flowing gases up to an overpressure of 303,975 Pa.

The prepared and characterized SC MOF was then used as a sensing element in the measurement setup shown in Fig. 3(a). Detailed setup of the SC MOF connected with lensed SMF (input PCE) via sealed SMA connectors is shown in Fig. 3(b). The gas mixing unit consisted of two input gas flow meters with a range of 0–500 cm^3/min. The toluene vapors were prepared by bubbling a constant flow of nitrogen into liquid toluene in a closed bubbler (pressure tank). The concentrations of toluene vapors were controlled by the flow of pure nitrogen in the gas mixing unit. The gas mixture was then injected into the specially developed fiber optic PCE. Whole measuring system was kept at a constant temperature of 23 °C and all measurements were done at this temperature.

The operational reversibility of the SC MOF in time was also tested. A mixture of toluene vapors with the concentration of 0.2 mol% in nitrogen was injected into the SC MOF. Temporal changes in the output power were measured at the end face of the SC MOF at the constant temperature of 23 °C, an overpressure of 101.325 kPa (1 atm), and a flow rate of 15.46 μl/min.

The molar fraction of the toluene vapors in nitrogen was calculated from the mass-flow balance relationship:

$$X_{tol} = \frac{\dot{n}_{tol}}{\dot{n}_{tol} + \dot{n}_{tol-N_2} + \dot{n}_{N_2}} \quad (1)$$

where $\dot{n}_{tol}$ is the toluene molar mass flow, $\dot{n}_{tol-N_2}$ is the nitrogen molar mass flow through the bubbler and $\dot{n}_{N_2}$ is the nitrogen molar

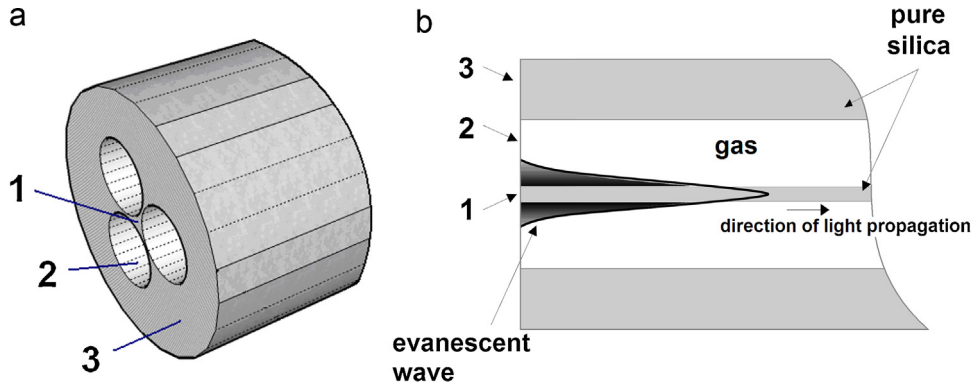

Fig. 1. SC MOF structure: (1) core area; (2) cladding holes; (3) outer jacket. (a) Cross section of the SC MOF; (b) longitudinal section of the SC MOF showing the evanescent wave of the guided mode in the core of the fiber.