# Optical fiber methane sensor based on SAN film containing cryptophane-E-$(OEt)_6$

**Guangqin Zhu (朱广琴)[1], Xueming Li (黎学明)[1,2*], Chuanyi Tao (陶传义)[2], Jing Huang (黄 静)[2], and Jianchun Yang (杨建春)[2]**

[1]*College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China*

[2]*Key Laboratory of Optoelectronic Technology and Systems, Ministry of Education, College of Optoelectronic Engineering, Chongqing University, Chongqing 400044, China*

[*]*Corresponding author: xuemingli@cqu.edu.cn*

Received March 10, 2012; accepted May 17, 2012; posted online August 3, 2012

A novel long-period fiber grating (LPFG) film methane sensor is designed and applied successfully. The sensor is constructed by depositing a thin styrene-acrylonitrile (SAN) film containing the new compound cryptophane-E-$(OEt)_6$ onto the cladding surface of the LPFG. This film is sensitive to methane gas. Methane causes a change in the refractive index of the sensing film, which can be measured by shifting the resonance wavelength. Experimental results show that the resonant wavelength shifts to the longer wavelength, with increasing methane concentration at a range of 0.0%–3.5% (v/v). A linear relationship is obtained within the test range. Detection limit is estimated at 0.2%, and response time is 60 s. No significant interference is detected from dry air, $O_2$, CO, $CO_2$, and $H_2$. This novel methane sensing material has great application potential due to its advantages.

*OCIS codes:* 060.2370, 130.6010, 120.1880.

*doi: 10.3788/COL201210.100601.*

Optical fiber gas sensor design has attracted considerable attention in recent years due to its high sensitivity, fast response, and immunity from electromagnetic influence as well as combustion and explosion[1]. The combination of optical fibers and cryptophane molecules for methane detection has become a significant advantage in several fields, such as coal-mine explosion-proof environments[2,3]. In recent years, an evanescent wave $CH_4$ sensor has been fabricated, in which cryptophane-A is deposited onto optical fiber. Unfortunately, the $CH_4$ detection limit for this sensor remains as high as 2% (v/v) [4]. The mode-filtered light sensor based on cryptophane-A, with the detection limit of 0.06%, has been applied to determine $CH_4$ samples; however response time is as long as 5 min[5]. Long-period fiber grating (LPFG) gas sensor for methane detection has been reported in previous studies. Styrene-acrylonitrile (SAN) film incorporated with cryptophane-A has been constructed onto the long-period grating of this sensor. The LPFG sensor has a detection limit of about 0.2%, a slope of 0.375 ($nm\%^{-1}$), and response time of 50 s[6]. Cryptophane-E, which has a larger cavity of three $O(CH_2)_3O$ bridges, is a new type of cryptophanes. This compound prefers to bind with $CHCl_3$, and is almost insensitive because its cavity is larger than that of cryptophane-A[7,8].

A new cryptophane-E-$(OEt)_6$ host with smaller inner windows was synthesized in this letter. A total of 6 larger ethoxy substituents were used to replace the 6 methoxy groups of cryptophane-E[9]. A novel LPFG methane sensor based on a thin SAN film that contained a new cryptophane-E-$(OEt)_6$ host was constructed. Sensing performance was also evaluated.

The effect of the refractive index of sensing film on resonant wavelength shift was analyzed based on the triple-clad LPFG model[10]. The LPFG couples the light from the forward propagating mode of the core to a discrete set of co-propagating cladding modes at the wavelengths governed by the phase matching condition given by

$$\lambda_{\rm res} = (n_{\rm co} - n_{\rm cl(\nu)})\Lambda, \nu = 1,\ 2,\ 3,\ \cdots, \qquad (1)$$

where $\lambda_{\rm res}$ is the resonant wavelength, $\Lambda$ is the grating period, and $n_{\rm co}$ and $n_{\rm cl(\nu)}$ are the effective indices of the fundamental core mode and the $\nu$th cladding mode of the fiber, respectively. The original resonant wavelength $\lambda$ and the grating period $\Lambda$ in this work are at 1 538 nm and 520 $\mu$m, respectively. Typically, the change in the effective index of sensing film containing cryptophane-E-$(OEt)_6$ is induced by methane in close vicinity to the surface, whereas the change in the refractive index is measured as a shift in resonance wavelength. Methane is selectively encapsulated by cryptophane-E-$(OEt)_6$ when it is introduced to the sensor. This mechanism changes the refractive index of cladding, resulting in the change of resonance wavelength. The value of methane concentration is then obtained from the wavelength shift.

In this letter, cryptophane-E-$(OEt)_6$ was synthesized from the starting material, ethyl vanillin (3-ethoxy-4-hydroxybenzaldehyde), in accordance with the direct method (Fig. 1). This method is similar to cryptophane-E synthesis[11]. The following $^1$H-NMR ($CDCl_3$) data for cryptophane-E-$(OEt)_6$ were acquired:$^1$H-NMR ($CDCl_3$, $\delta$, ppm), 6.91 to 6.87 (s, 12H, Ar), 4.67 (d, 6H, CHa), 4.24 (s, 4H, $OCH_2CH_3$), 4.04 (s, 4H, $OCH_2CH_2$), 3.47 (d, 6H, CHe), 2.08 (m, 12H, $CH_2$), and 1.26 (s, 18H, $CH_3$). Anal.Calcd for $C_{63}H_{72}O_{12}$: C, 74.09; H, 7.11; O, 18.80. Found: C, 74.12; H, 7.03; O, 18.75. A SAN film that contained cryptophane-E-$(OEt)_6$ was deposited on the long-period grating (around 20-mm length) through the dip-coating technique[11,12]. The SAN solution that contained cryptophane-E-$(OEt)_6$ was obtained by dissolving 1.0 g of SAN in 20-ml solution of tetrahydrofuran (THF), followed by a mixture comprising 300-mg powder

 © 2012 Chinese Optics Letters

of cryptophane-E-$(OEt)_6$. Afterwards, the mixture was deposited onto the optical fiber grating surface. The cladding area of the fiber grating was first cleaned using distilled water, pure ethanol and acetone, and then placed in a vacuum drying closet at 60° for 20 min. This process was completed using the dip-coating method, where the fiber was immersed into the SAN containing the cryptophane-E-$(OEt)_6$ solution at a dipping rate of about 2 mm/s[11]. A typical cross-section scanning electron microscope (SEM) (VEGA II LMU, TESCAN) image of the LPFG coated with the SAN film containing cryptophane-E-$(OEt)_6$ is shown in Fig. 2. A thickness of ∼500 nm is observed. The radii of the core and the cladding are 4.15 and 62.5 $\mu$m, respectively. Therefore, the radii of the LPFG coated with SAN films, including cryptophane-E-$(OEt)_6$, is 63.0 $\mu$m.

Figure 3 shows the schematic diagram of the experimental setup. In our experiment, two mass flow controllers precisely controlled the flow of the methane and nitrogen carrier gas. The LPFG sensor was placed in the center of the gas chamber, in which the gases were mixed by the stainless steel helical tube between the controllers and the chamber. The ends of the long-period grating optical fiber were respectively connected to an optical spectrum analyzer (OSA) (Agilent 86140B) and the superluminescent diode (SLD) light source, which consisted of a 2-mW SLD with a central wavelength of ∼1 550 nm and a bandwidth of ∼40 nm (Dense Light Co., Ltd.).

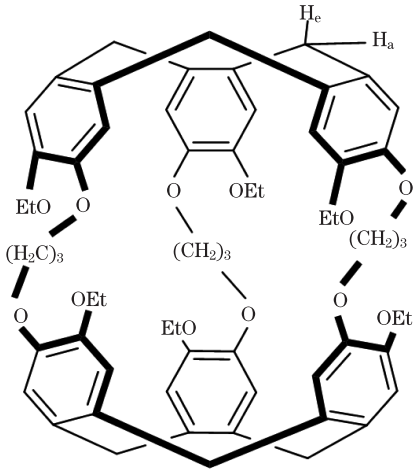


Fig. 1. Chemical structure of cryptophane-E-$(OEt)_6$.

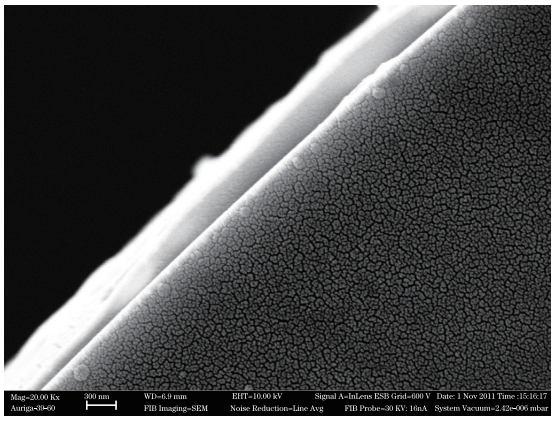

Fig. 2. SEM micrograph of the cross-section of the fiber coated with the thin film which contains cryptophane-E-$(OEt)_6$.

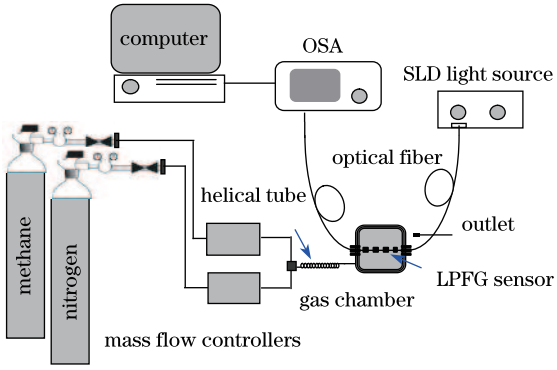


Fig. 3. Experimental setup for methane detection.

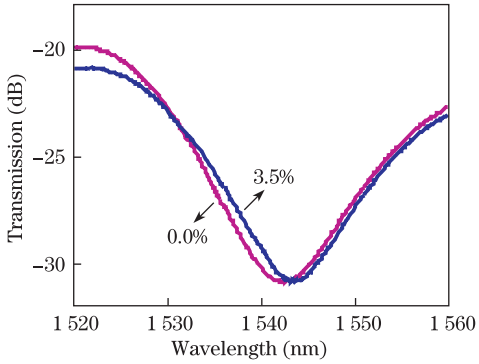


Fig. 4. Transmission spectra of the sensor before and after methane exposure.

The prepared LPFG was exposed directly to various concentrations of methane gas in the gas chamber in order to evaluate the sensing performance of the methane sensor.

Figure 4 presents the transmission spectra of the LPFG sensor when exposed to gas with methane concentrations of 0.0% and 3.5%. The resonant wavelength shifts from 1 542.48 to 1 543.60 nm. Meanwhile, Fig. 5 shows the calibration curve between wavelength shifts (sensor response) and the methane concentration. The calibration curve indicates the relationship between the resonant wavelength shift and the methane concentration that ranges from 0.0% to 3.5%. A linear relationship is obtained within this range, with a slope of 0.297 (nm%$^{-1}$) and a correlation coefficient ($R^2$) of 0.990. The detection limit is 0.2%. Given that the LPFG sensor was exposed to a fixed methane concentration, the change of resonant wavelength was investigated to verify the reversibility of the LPFG sensor and measure the sensor response time. Figure 6 shows the wavelength shifts versus time of the LPFG sensor when it has been exposed repeatedly to pure nitrogen and methane concentrations of 0.5% or 3.5%. The shifts stabilized after about 60 s, and another 60 s is required to return to the original state. Hence, sensor response time is 60 s.

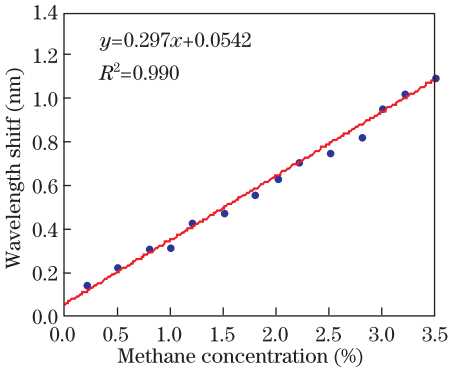


Fig. 5. Calibration curve between wavelength shifts and methane concentration.

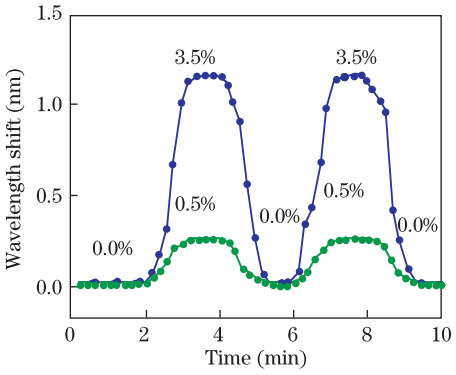


Fig. 6. Sensor signals upon repeated exposure to pure nitrogen and to fixed methane concentrations of 0.5% or 3.5%, respectively.

To investigate its selectivity, the LPFG sensor was exposed respectively to different gases, such as $N_2$ (99.99%), dry air, $O_2$ (99.99%), CO (99.95%), $CO_2$ (99.95%), and $H_2$ (99.99%). These gases do not cause sensor response obviously; in comparison, $CH_4$ has good responsiveness, indicating that the LPFG sensor has impressive methane discrimination abilities among different gases.

In conclusion, a LPFG film sensor deposited with thin SAN film that contains the new compound cryptophane-E-$(OEt)_6$ for methane detection is applied successfully. The LPFG sensor has great sensitivity to methane concentrations ranging from 0.2% to 3.5% by volume. A linear relationship is obtained within this range. A detection limit of about 0.2% is estimated, and a response time is recorded at 60 s. The gas sensor is almost unresponsive to dry air, $O_2$, CO, $CO_2$, and $H_2$, but is highly sensitive to $CH_4$. The sensor for methane detection is sensitive, simple in structure, and entails low-cost fabrication, and has excellent performance. The new sensor is ideal for the detection of methane and can be potentially used in further practical applications.

This work was supported by the National Natural Science Foundation of China (No. 60871039), the Natural Science Foundation Project of Chongqing (No. 2010BB4246). and the Science and Technology Development Project of Chongqing (No. CSTC2012ggyyis 9007), the Sharing Fund of Chongqing University′s Large-Scale Equipment.

## References

1. S. Wang, R. Chen, J. Liu, and Y. Wang, Semicond. Photon. Technol. **10,** 141 (2004).
2. J. Yang, L. Xu, and W. Chen, Chin. Opt. Lett. **8,** 482 (2010).
3. C. Tao, X. Li, J. Yang, and Y. Shi, Sens. Actuators B: Chem. **156,** 553 (2011).
4. M. Benounis, N. Jaffrezic-Renault, J.-P. Dutasta, K. Cherif, and A. Abdelghani, Sens. Actuators B: Chem. **107,** 32 (2005).
5. S. Wu, Y. Zhang, Z. Li, S. Shuang, C. Dong, and M. M. F. Choi, Anal. Chim. Acta. **633,** 238 (2009).
6. C. Zhang, W. Shen, R. Fan, G. Zhang, S. Shuang, C. Dong, and M. M. F. Choi, Spectrochim. Acta Mol. Biomol. Spectros. **75,** 157 (2010).
7. J. Canceill, L. Lacombe, and A. Collet, J. Am. Chem. Soc. **108,** 4230 (1986).
8. J. Canceill, M. Cesario, A. Collet, J. Guilhem, L. Lacombe, B. Lozach, and C. Pascard, Angew. Chem. Int. Ed. Engl. **28,** 1246 (1989).
9. J. Canceill, L. Lacombe, and A. Collet, J. Chem. Soc. Chem. Commun. **3,** 219 (1987).
10. J. Yang, C. Tao, X. Li, G. Zhu, and W. Chen, Opt. Express **19,** 14696 (2011).
11. M. Benounis, N. Jaffrezic-Renault, J.-P. Dutasta, K. Cherif, and A. Abdelghani, Sens. Actuators B **107,** 32 (2005).
12. S. Korposh, S. W. James, S.-W. Lee, S. Topliss, S. C. Cheung, W. J. Batty, and R. P. Tatam, Opt. Express **18,** 13227 (2010).