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Optical fiber Fabry–Perot interferometer with pH sensitive hydrogel film for hazardous gases sensing

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ABSTRACT

An optical fiber Fabry–Perot interferometer (FPI) coated with polyvinyl alcohol/poly-acrylic acid (PVA/PAA) hydrogel film for toxic gases measurement has been developed. The FPI consists of a short section of hollow core fiber sandwiched by two single mode fibers. Dip-coated pH-sensitive PVA/PAA hydrogel film on the fiber end performs as a receptor for binding of volatile acids or ammonia, which makes the sensing film swelling or shrinking, which results in the dip wavelength shift of the FPI. By demodulating the evolution of reflection spectrum for various concentrations of volatile acids, a sensitivity of 20.8 nm/ppm is achieved with uniform linearity.

Keywords: optical fiber; polyvinyl alcohol; poly-acrylic acid; gas sensor.

1. INTRODUCTION

Hazardous gases monitoring in real time, such as ammonia, acetic acid and volatile organic compounds, is a critical issue in enclosed environment. Fiber optic gas sensors have been receiving more and more attention due to their inherent characteristics, such as immunity to electromagnetic interference, small size and low cost etc. For the purpose of chemical and biological applications, the optical fiber sensors are usually functionalized with sensing film/membrane for sensitivity or specificity enhancement. Therefore, in order to realize hazardous gases sensing, the sensing films with immobilized pH indicators, which undergoes a suitable absorbance or fluorescence intensity change when exposed to volatile acids/bases, can be employed for detection [1-4]. The traditional indicators based optical fiber gas sensors are mainly intensity demodulation. The technique is cost-effective and reliable but it is prone to error due to excitation light intensity fluctuation, leaching of indicator and typically has a short self-life.

In this study, the cross-linked polymer composed of poly (acrylic acid) (PAA) and polyvinyl alcohol (PVA) is employed to functionalize optical fiber Fabry-Perot interferometer (FPI) for hazardous gas detection. Attribute to intrinsic properties of the PVA/PAA hydrogel, its volume changes considerably in various pH levels [5], which in turns, modulates the effective optical cavity length of the FPI resulting in the spectrum shift. As a result, concentration of volatile acids or bases can be determined by demodulating the wavelength shift of the FPI. The proposed sensor not only exhibits a good sensitivity and stability, but also offers easy fabrication, compact structure and most importantly low cost.

2. SENSOR PRINCIPLE AND FABRICATION

The schematic diagram of the proposed sensor is presented in Figure 1 (a). The sensor consists of two different types of fibers: single mode fiber (SMF) with the core refractive index (RI) $n_{SMF}\approx1.45$ and hollow core fiber (HCF) with the core RI of $n_{HCF}\approx1$, respectively. The sensor consists of three reflective surfaces, labeled as reflection reflector R_1, R_2 and R3 in Figure 1(a), respectively. These reflectors form three Fabry-Perot cavities, which are, R_1-R_2, R_2-R_3 and R_1-R_3 and the round-trip propagation phase shift for individual cavity are [6, 7]: $\phi_1=4\pi n_{HCF}L_1/\lambda$, $\phi_2=4\pi n_{SMF}L_2/\lambda$, $\phi_3=\phi_1+\phi_2=4\pi(n_{HCF}L_1+$

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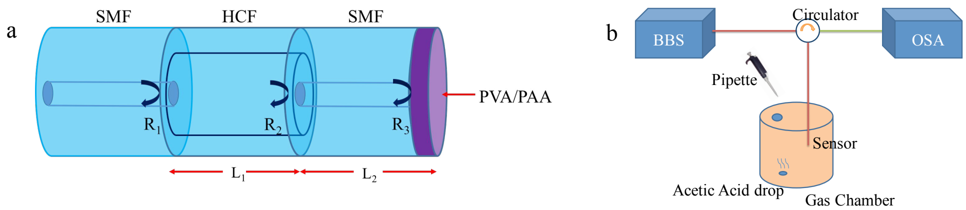

Figure 1 a. Experiment setup for hazardous gas sensing b. Schematic diagram of the FPI sensor

$n_{SMF}L_2)/\lambda$, where L_1 and L_2 are the cavity length of the region R_1-R_2 and R_2-R_3 respectively and λ is the free space optical wavelength. The effective length $L_{eff1}=n_{NCF}L_1$ of first cavity (R_1-R_2), which is filled with air and considered to be constant ($n_{HCF}=1$) as it will not be influenced by the pH various.

To facilitate volatile organic compounds response, the proposed sensor was functionalized with PVA/PAA hydrogel at the end face of the sensor. The PVA/PAA hydrogel sensing film is a pH sensitive polymer and the sensitivity is relied on the polyelectrolyte (acrylic acid) components presented in the polymeric networks. At the beginning, carboxylic acid groups in PAA are deprotonated when the pH in the medium film is larger than pKa (~4.28) values conditions as $[RCOOH]_{gel} + [OH^-]_{aq} \rightarrow [RCOO^-]_{gel} + H_2O$. Therefore, the acid groups contained in the polymer network are ionized and generate mobile counter ions inside the gel. These charged ions lead the hydrogel swelling due to electrostatic repulsion. As the amount of H+ increase, which lead the pH value in the hydrogel become smaller than the pKa values, the acidic group protonates $[RCOO^-]_{gel} + [H^+]_{aq} \rightarrow [RCOOH]_{gel}$, so the amount of the mobile counter ions decrease result in gel shrinking [5]. Therefore, base on this pH dependent swelling property, the gaseous acetic acid sensing can be realized as hydrogen ion H^+ will be produced when gaseous acetic acid meet water vapor trapped in the PVA/PAA hydrogel film $CH_3COOH \leftrightarrow CH_3COO^- + H^+$. The amount of the H^+ will in turn change the pH value inside the hydrogel and swelling/shrinking effects take place. Therefore, the cavities of the sensor will be modulated when the hazardous gases concentration is varied.

Since $\phi_3 = \phi_1 + \phi_2$ and ϕ_1 is constant, the value of ϕ_3 changes only with that of ϕ_2. Calculated from ϕ_2, it is assumed that the wavelength of the resonance dip λ_m in the reflection spectrum satisfies $4\pi n_{SMF}L_2/\lambda_m=2m\pi$, where m is integer. So λ_m can be expressed by $\lambda_m=2n_{SMF}L_2/m$. When the FPI is exposed to different concentration of hazards gas, the volume of hydrogel will vary and vary the effective cavity length $\Delta L_{eff2}=\Delta(n_{SMF}L_2)$. This in turn generates wavelength shifts, $\Delta\lambda_m$ which can be expressed by $\Delta\lambda=(\lambda_m/2L_{eff2})\Delta L_{eff2}$. As observed from this equation, the wavelength shift is a function of cavity length. When the pH sensitive hydrogel swells in the presence of volatile acids or bases, it causes the variation of the cavity length and thereby induces the phase shift of the FPI reflection spectrum. Thus the concentration of the hazardous gas can be detected by monitoring the spectrum wavelength shifts.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Various hollow-core fibers are employed in FPI fabrication and the majority is photonic crystal fibers (PCFs) [8-11]. PCFs are expensive and have multiple side holes, which are easily collapsed, in the vicinity to the splicing joint with SMF. This may significantly increase the reflection loss by destroying the light-guiding condition of PCFs near the joint interface. Thus, the HCF (Polymicro, TSP050150) with inner diameter 75 µm, which is several times larger than that of SMF core, was used to form the air cavity of FPI. Sumitomo Type-39 arc-fusion splicing machine was utilized for

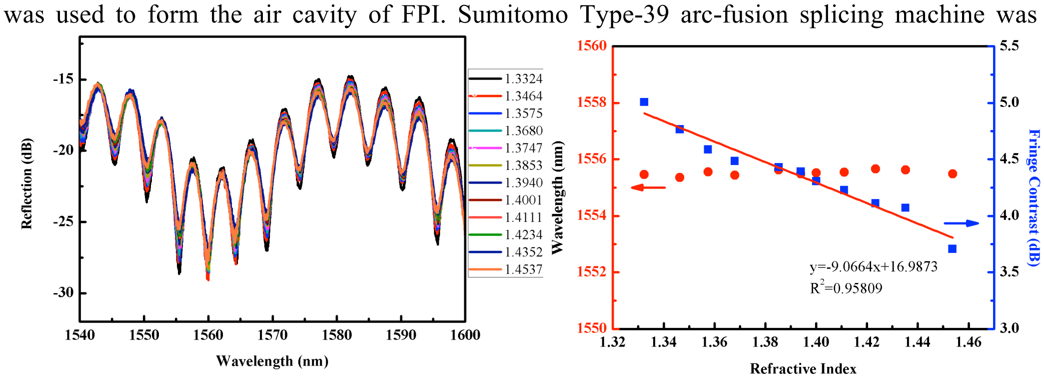

Figure 2 Fringe contrast and wavelength variation of FPI under different RI solutions

joining the SMF and HCF, after which, the other end of the HCF was cleaved to ~100 µm with aid of micro movement stage. Finally, the end face of the HCF was again spliced with another short section of SMF ~100 μm to complete Fabry-

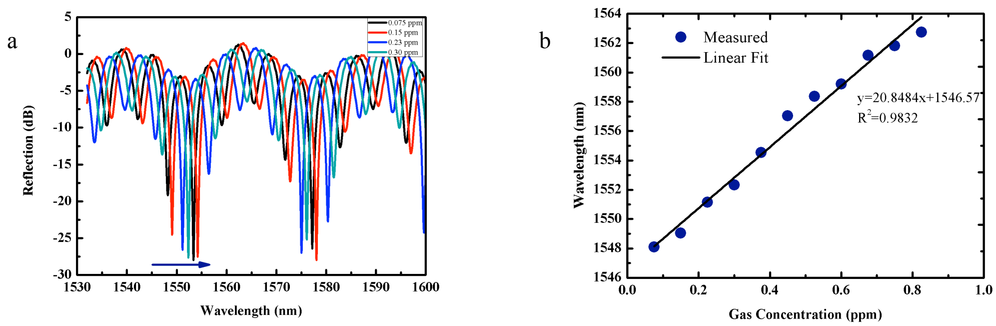

Figure 3 a. Reflection spectra of the FPI exposed to acetic acid vapor b. Wavelength shift upon the acetic acid vapor concentration

Perot compact structure. Prior to hydrogel functionalization, the RI response of the FPI was first tested. The FPI was secured vertically and immersed into different RI solutions tuned by different volume concentrations of glycerin in water. After testing in each RI solutions, the sensor was cleaned by pure water and dried with nitrogen gas. The spectra of the FPI in various external RI were shown in Figure 2. It can be seen that fringe contrast of FPI reflection spectrum decreases with the glycerin solution RI increases from 1.33 to 1.45. The decrease in interference spectrum contrast is caused by a closer RI difference between the SMF and external environment [12].

To fabricate the hydrogel, PVA of 15% (w/w) and PAA of 7.5% (w/w) were dissolved separately in deionized water at 90 ˚C with constant mixing. The two solutions were further mixed in a weight ratio of 8:2, PVA: PAA and stirred for 1 h at 60 ˚C. The FPI was dip-coated into the PVA/PAA mixture with a drawing speed of 15 mm/s. Subsequently, it was thermally cross-linked at 130 ◦C in an oven for 30 min, then the hydrogel was physically bounding on the fiber end [8].

The schematic illustration of the experimental setup used to evaluate the hydrogel coated FPI performance for volatile acids or bases is presented in Figure 1(b). The experiment setup consists of a broadband light source (BBS), optical fiber circulator and optical signal analyzer (OSA, YOKOGAWA AQ6370). The FPI was linked to the output of the optical fiber circulator. Light was guided to the FPI through the optical fiber circulator from the BBS. The OSA was employed to detect the reflected interference signal via the same circulator. The FPI was placed vertically in the middle of test chamber (volume ~15 L) and known quantities (~ 5 μl) of aqueous volatile acids or bases are injected to achieve various concentrations of vapor. The wavelength shift of the interference fringes was monitored and recorded using an OSA with a spectral range of 1530-1610 nm. During the experiment, 1 hour was given to the sealed chamber and hydrogel coated FPI to reach equilibrium at each volatile acids or bases level before recording.

The experimental spectra of the interferometer in various acetic acid gases concentration of 0.075 ppm, 0.15 ppm, 0.23 ppm and 0.30 ppm are illustrated in Figure 3(a). A significant wavelength shift of the interference fringes is observed, which shifts towards the longer wavelengths as concentration increases. The wavelength shift of the FPI under different acetic acid vapor concentration is presented in Figure 3(b), sensitivity of 20.85 nm/ppm was achieved. Similarly, the wavelength shift of the sensor in different concentration of ammonia is also shown in Figure 4. PAA is an efficient ammonia absorber due to presence of free carboxylic acid functional groups, leading to higher sensitivity toward amine compounds [13]. Comparing the response of the hydrogel coated FPI and bare FPI, the first exhibits wavelength modulation under different concentration acid gas while later shows intensity modulation towards different

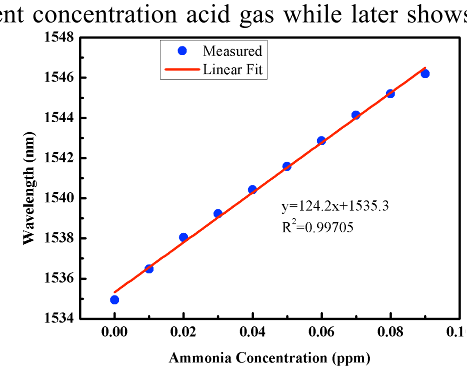

Figure 4 Wavelength shift upon the ammonia vapor concentration

RI solutions, indicating the spectrum of FPI response is mainly depend on the volume change of the hydrogel that, induces different effective cavity length. As observed in Figure 2 the contrast of the interference spectrum of the FPI changes insignificantly with concentration, further indicates that the RI variation of hydrogel is relative small in comparison to the volume change.

4. CONCLUSION

An enhanced sensitive fiber optic hazards gas sensor is fabricated and experimentally demonstrated by using thermal cross linked PVA/PAA hydrogel coated FPI. The PVA/PAA was selected as the coating agent to form a hybrid FPI due to its pH-dependent swelling/shrinking ability, which modulates the effective length of the FPI cavity. The acetic acid vapor is detected under 1 ppm by monitoring the wavelength shifts of the FPI fringes, the experimental results show that the sensor is able to detect small amount of volatile acids and bases with satisfactory stability. Due to miniature size of the PVA/PAA hydrogel coated FPI, a good sensitivity of 28.85 nm/ppm with low temperature cross sensitivity is achieved. Overall, the PVA/PAA hydrogel has proven itself to be a good candidate to form a fiber-optic based FPI for volatile acids and bases sensing application, as it offers good diaphragm forming ability, good mechanical rigidity and improved stability with respect to changes in hazards gas.

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