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High Sensitivity Ammonia Gas Sensor Based on a Silica-Gel-Coated Microfiber Coupler

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High sensitivity ammonia gas sensor based on a silica gel coated microfiber coupler

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***Abstract*—In this paper, a high sensitivity ammonia gas sensor is proposed based on a silica gel coated microfiber coupler (MFC). The MFC structure is formed by the two tapered fibers with 3 μm waist diameter each, which were fabricated by using a customized microheater brushing technique. Silica gel coating was prepared by a sol-gel technique and applied on the surface of the MFC as a thin layer. The spectral characteristics of the proposed sensor were studied under various ammonia gas concentrations. The experimental results show that the coating thickness strongly affected the sensitivity of the MFC-based sensor to ammonia gas concentration. For the sensor with a 90 nm silica gel coating thickness, the highest measurement sensitivity is 2.23 nm/ppm for ammonia gas concentration, and the resolution is as good as 5 ppb, while the measured response and recovery times are about 50 and 35 seconds, respectively. Finally, it is demonstrated that the proposed sensor offers good repeatability and selectivity to ammonia.**

***Index Terms*—optical fiber sensors, microfiber coupler, ammonia gas sensor.**

I. Introduction

AMMONIA (NH_3) has been extensively used in many areas such as industrial coolant systems, fertilizer production, and clinical diagnostics [1-3]. However, even low concentrations of NH_3 may pose a hazard to human health. In addition recently, the possibility of using ammonia as a disease indicator has attracted a lot of attentions [4]. The atypical concentrations of ammonia in the blood, feces, exhaled breath, and skin could serve as biomarkers of certain diseases [5]. Due to the growing importance of detection of gaseous ammonia both for diagnostics and health hazards prevention, highly sensitive and selective ammonia sensors have been widely studied. Several techniques to detect ammonia gas have been proposed to date, such as metal oxide semiconductor detectors, infrared gas analyzers, chromatography-mass spectrometry, and optical fiber based sensors. However, the metal oxide semiconductor detectors exhibit enhanced sensitivity only at high temperatures, and also suffer from the poor selectivity [6]. Infrared gas analyzers have the disadvantages of being expensive and bulky [7]. Chromatography-mass spectrometry is another alternative but it has significant limitations as it involves time consuming analysis, expensive instruments, and the requirement for experienced operators [8]. Among these techniques, optical fiber based sensors have several advantages such as immunity to electromagnetic interference, operation at room temperature, low cost fabrication, long life time, and a capability for remote sensing [9, 10].

Typically optical fiber based sensors utilize specific coating materials to detect ammonia gas. For example, silica has chemisorption with ammonia [11] and its refractive index (RI) changes as a result of the chemisorption, which offers the possibility of using silica gel as the coating material for fiber optic refractometric sensors. Tao et al. [12] developed an optical fiber probe for sensing ammonia in gas samples and in water by coating an organic dye immobilized porous silica membrane on the surface of a bent optical fiber core. However, due to the presence of organic dye, the sensor has a significant drawback of limited lifetime. Guo et al. [13] proposed an ammonia gas sensor with silver doped silica nanocomposite coated on the surface of a bent optical fiber. However, the sensor suffers from the limitation of low tolerance to the presence of ultraviolet light. Adding or immobilizing other materials on silica surface can lead to limitations similar to those mentioned above. However, pure silica gel is a good candidate for a coating material, offering the advantages of easy application on the surface of optical fibers due to its moderate viscosity and the refractive index match between the silica gel and the optical fiber surface, a long lifetime for the material itself and low absorption in a wide wavelength range. Thus, we selected a pure silica gel as the coating material for the proposed sensor.

Optical microfiber couplers (MFCs) are shown to be sensitive to environment RI changes [14, 15]. The use of a fiber tapering process enables a considerable fraction of the power propagating in the fiber to be contained in an evanescent field, which ensures strong interaction between light transmitted through a tapered fiber and its surrounding environment [16]. Moreover, using an MFC structure as a sensor offers an even

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higher sensitivity compared to that of a single microfiber taper because for an MFC the environment influences not just a single evanescent field but the coupling between two evanescent fields of the weakly fused fiber tapers [17]. Furthermore, compared to other optical elements based on mode coupling, such as a microsphere resonator or a singlemode - multimode - singlemode fiber structure, the MFC structure has the advantages of a larger evanescent field, along with ease of operation and interconnection to other fibers [18]. "Zhang et al. [19] developed an ammonia gas sensor based on a graphene-coated microfiber Bragg grating structures. However, the fabrication process for the used structure is much more complicated compared to that of microfiber coupler, and the sensitivity of such a sensor was only 6 pm/ppm. Pawar et al. [20] proposed an ammonia gas sensor by using highly porous graphene coated optical fiber in Fabry-Perot interferometric configuration, but the sensitivity of such a sensor to ammonia was only 20 pm/ppm."

In this paper, we propose and demonstrate a highly sensitive ammonia gas sensor based on a silica gel coated MFC. Experimental results show that the increase of the coating thickness leads to higher sensitivity. For the proposed MFC based sensor, formed by two weakly fused fiber tapers with 3 μm waist diameter for each fiber and a 90 nm coating thickness for the silica gel, the spectral dips in the transmission spectrum experience a nonlinear blue shift with the increase of ammonia gas concentration in the surrounding air. The highest measurement sensitivity is 2.23 nm/ppm for ammonia gas concentration and the resolution is as good as 5 ppb, while the measured response and recovery times are about 50 and 35 seconds, respectively. Good repeatability and selectivity are demonstrated, which indicate the potential of the proposed sensor for industrial and other ammonia gas detection applications.

II. EXPERIMENT

1. Preparation of the Microfiber Coupler

The MFC was fabricated by tapering and fusing two fibers together at the same time using a method known as the microheater brushing technique [21]. Fig. 1 shows the schematic diagram of the MFC. The fabricated MFC had a total length of 25 mm which included a 3 mm long uniform waist region in the center and two 11 mm long transition regions at each end. The waist region is formed by two weakly fused microfibers each with a 3 μm diameter. The weakly fused condition is important because the coupling coefficient has a stronger dependence on the surround RI change when the coupler is weakly fused [22]. In the experiment, port 1 of the MFC was connected to a broadband amplified spontaneous emission source (Fiber Coupled SLD, Thorlabs), and port 4 was connected to an optical spectrum analyzer (OSA) (86142B, Agilent). The measured transmission spectrum of the MFC sample is shown in Fig. 2.

Coupled mode theory, which assumes that an MFC is made by fusing two single-mode microfibers with a uniform shape and homogenous RI profiles, can be used for analyzing the coupling behavior for an MFC [23]. Based on the theory, the two microfibers work together as a composite system to support the propagation of an even mode and odd mode. The interference between the odd-even modes results in a periodic interchange of the guided mode power, which leads to the transmission spectrum displaying a semi-periodically resonant behavior at each of the output ports.

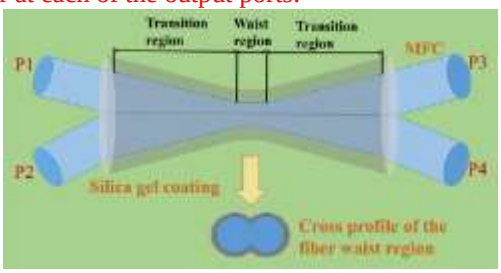


Fig. 1.Schematic diagram of an MFC.

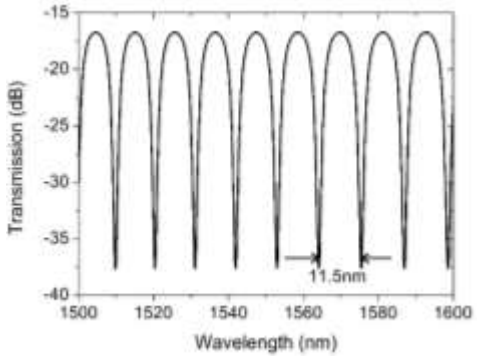


Fig. 2. Transmission spectrum of the designed MFC.

2. Preparation of the Ammonia Sensor

In this work, in order to investigate the influence of coating thickness on the sensitivity, the coating thickness was varied by a combination of applying silica gels with different viscosity and by changing the number of coating cycles. The silica sol solution used in our experiment was prepared as follows. 10 ml of tetraethylothosilicate (TEOS) was mixed with 5 ml of ethanol for 20 minutes using a magnetic stirrer and subsequently 1.5 ml of a 0.1 mol/l H2SO4 solution was added to the mixture and stirred. Three silica sol solutions with different viscosities were fabricated through stirring the silica sol solution for mixture 100, 150, and 180 minutes, respectively, and labeled as S-1, S-2, and S-3 sample. Since in our experiments, the stirring was taken in open environments (no sealing to prevent water evaporation), resulting in larger amount of water evaporation for longer stirring time. In this case silica gel S-3 sample had the highest viscosity, resulting in the thickest coating layer [24], while the S-1 sample had the lowest viscosity and resulted in the thinnest coating layers.

The sample sensor was fabricated by passing a drop of silica gel through the MFC using a motor controlled translation stage. A single-layer coating was defined as a single pass of the silica drop from one side of the MFC to the other side. The coating length of a single-layer coating is 25 mm. By repeating the single pass coating progress, different layers of silica coating can be realized. When the desired coating cycles were

completed, the coated fiber sensor was cured at room temperature for 48 hours. The MFC sample sensor coated with 3-layers of S-3 was examined by using a Scanning Electron Microscope (SEM) as shown in Fig. 3. The coating thickness of the silica gel is estimated to be 90 nm.

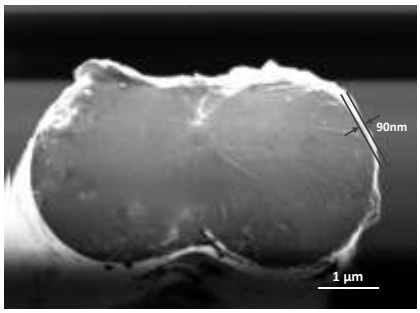


Fig. 3. SEM image of the cross section of the silica gel coated tapered MFC.

3. Ammonia sensing experimental setup

The customized glass-made gas chamber was formed by a movable cover and a fixed base. The silica gel coated MFC sensor was fixed at one side of the customized gas chamber and connected to the ASE through a polarization controller (PC) and OSA, as shown in Fig. 4. Ammonia solution was injected into the chamber through the transom window and allowed to evaporate inside the chamber to reach a desired ammonia gas concentration. All experiments were carried out at room temperature (17 °C). The resulting ammonia gas concentrations were calculated based on its concentration in the liquid solution and volume of the chamber, in a manner similar to the method reported in [25].

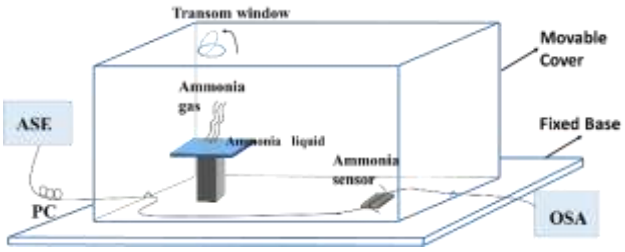
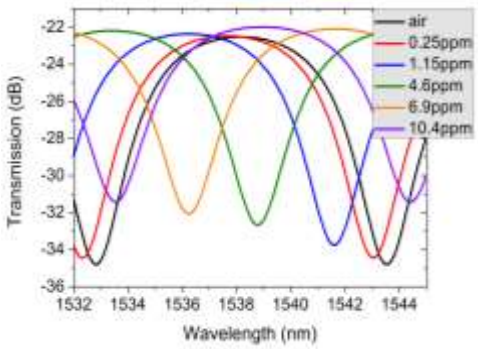


Fig. 4. Experimental setup for ammonia gas sensing.

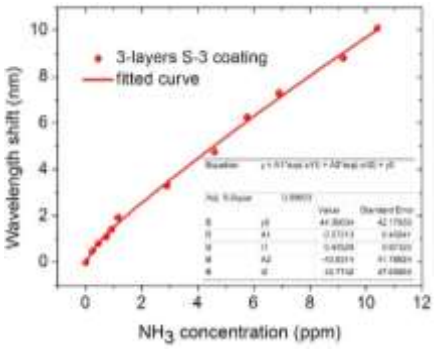
III. Results and Discussion

1. Sensing Performance

For the sensor sample coated with three layers of silica gel S-3, Fig. 5(a) shows the measured spectral responses at different ammonia gas concentrations in the chamber. As seen from the graph, the spectral dips show a monotonic blue-shift when the ammonia gas concentration increases. This phenomenon can be explained as follows. When the surrounding ammonia gas concentration increases, the ammonia molecules from the air diffuse into the silica material and undergo chemisorption, which thus causes an increase in the refractive index of the silica coating on the MFC surface. A similar effect was reported in [26], where an increase in the surrounding refractive index resulted in a blue-shift of the MFC spectrum. Fig. 5(b) shows the absolute value of the measured dip wavelength shift versus ammonia concentration. It is worth mentioning that in this work, the dip wavelength shift is defined as the 3 dB average value of the selected spectral dip in the MFC spectrum. This method is more reliable than tracking of the central dip wavelength. As can be seen from the graph, the experimental data for the wavelength shift versus ammonia concentration fits well with an exponential function, which indicates that the proposed sensor has a higher sensitivity and better resolution at lower concentrations. The wavelength shift is 10.1 nm when the ammonia gas concentration changes from 0 to 10.4 ppm. The highest sensitivity is 2.23 nm/ppm when the concentration varies from 0 to 0.25 ppm. Assuming a typical spectral resolution of the OSA is 0.01 nm, the resolution for the proposed sensor could be as low as 5 ppb.



(a)



(b)

Fig. 5 (a). Measured spectral responses at different ammonia gas concentrations for the MFC coated with 3 layers of S-3. (b) Measured dip wavelength shift vs. ammonia gas concentration.

The response and recovery times of the sample sensor coated with three layers of S-3 are shown in Fig. 6. The response time is defined as the time interval between the injection of the ammonia in the chamber to the point when the sensor's response reaches up to 90% of its full response, and recovery time is defined as the time interval between the start of the evacuation of ammonia from the chamber to the point when the sensor's response reaches 90% of the full recovery. The response and recovery times are found to be about 50 and 35 seconds, respectively.

Moreover, it should be noted that in accordance with this definition the response times include, for example in the case of the rise time, the time taken for the ammonia solution to evaporate and ammonia gas to diffuse throughout the chamber

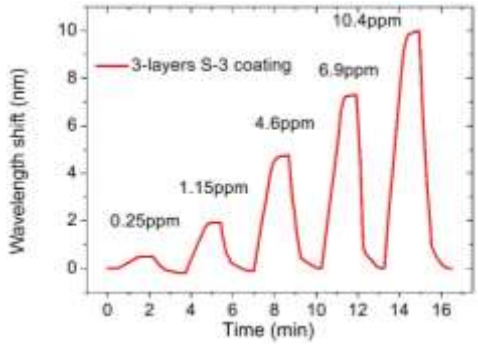
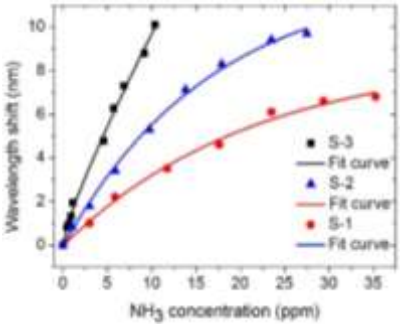


Fig. 6. The response and recovery of the sensor sample coated with 3 layers of silica gel S-3.

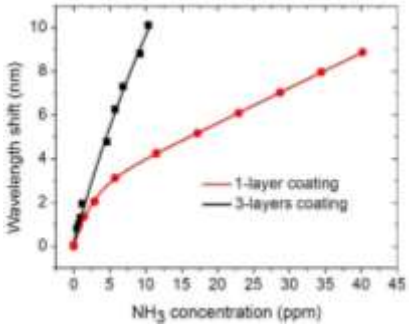
in addition to the sensor's response time. It is likely therefore that the actual sensors response times alone are significantly shorter. Test results also demonstrate that after sufficient recovery time, the spectral dip of the sensor fully returns back to the original wavelength position before the stimulus, demonstrating a good repeatability.

2. Effect of Coating Thickness

To investigate the influence of silica gel coating thickness on the sensitivity of the proposed sensor to ammonia gas, we carried out a series of experiments as follows. Fig. 7(a) shows the measured absolute value of the dip wavelength shift as a function of ammonia gas concentration for the three different MFC samples of the same diameter coated in each case with three layers of silica gels of different viscosity (S-1, S-2, and S-3) to realize coatings with different thickness. It can be seen from the graph that a thicker silica coating leads to a significantly enhanced sensitivity to ammonia concentration. Increasing the thickness of the silica coating leads to an increased absorption of ammonia gas, resulting in a larger refractive index change of the silica coating, and thus a larger wavelength shift. It should be noted that all the three sample sensors demonstrate a non-linear behavior with the increase of ammonia gas concentration and higher sensitivity at lower ammonia concentrations. Fig. 7(b) shows the wavelength dip shift as a function of ammonia gas concentration for the MFC coated with one and three layers of S-3 silica gel. The results confirm that an increase in the coating thickness leads to an increased sensitivity.



(a)

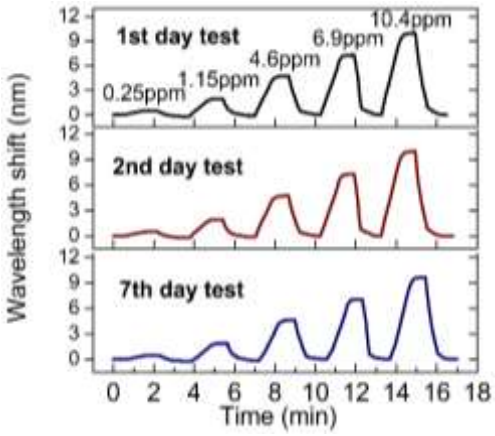


(b)

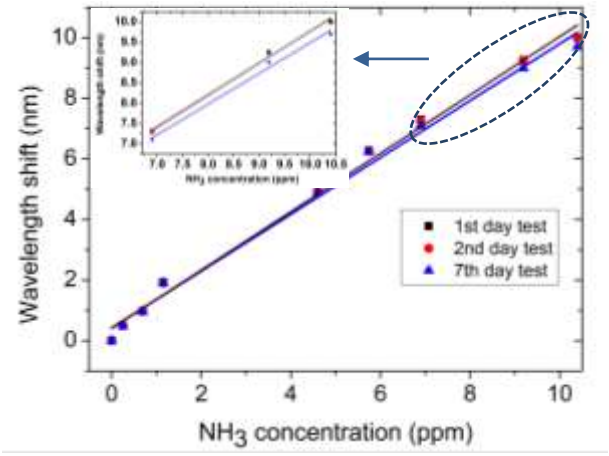
Fig. 7. (a) Measured dip wavelength shift of the MFC coated with 3 layers of silica coating as a function of ammonia gas concentration for samples coated with S-1, S-2 and S-3 silica gels. (b) Measured wavelength shift vs. NH_3 concentration for the MFC coated with S-3 silica gel for the two different numbers of coating cycles (1-layer and 3-layers).

3. Sensor repeatability

The repeatability of the proposed ammonia sensor was also investigated, as shown in Fig. 8. The sensor under study is the MFC coated with three layers of S-3 silica gel. The first day test was carried out on the day the sensor sample was fabricated, followed by the tests conducted one and seven days later (the 2nd and the 7th day tests, respectively). Fig. 8(a) shows the response and recovery times of the sensor as a function of step increases in the ammonia gas concentration on the 1st, 2nd, and 7th days since its fabrication, Fig. 8(b) shows the wavelength shift versus ammonia gas concentration for the three different test and the inset shows the zoomed section of the NH_3 concentration from 6.9 to 10.4 ppm. It is evident that the sensor exhibits good repeatability. The value of the wavelength shift remained the same during the 1st day and the 2nd day tests, and had a 3% decrement during the 7th day test. The difference in response and recovery times is about 0.7% between the 2nd day test and the 1st day test and about 1.7% between the 7th day and the 1st day tests. The slight variation in the sensor's performance over the period is most likely due to slight degradation of the coating over the 7 days period, for example, some of the silica coating on the MFC surface may have dropped off or possibly the chemical properties of the silica gel changed due to dust or other contaminants accumulation on the MFC surface.



(a)



(b)

Fig. 8. Repeatability tests for the sensor samples based on the MFC coated with 3-layers of S-3. (a) The response and recovery time of the sensor. (b) Measured wavelength shift vs. NH_3 concentration, the inset showing the zoomed relationship between wavelength shift and NH_3 concentration.

4. Sensor's selectivity to ammonia

It is well known that a good selectivity is an important factor for a practical gas sensor. Fig. 9 shows the results of our study of the selectivity of the proposed sensor to ammonia. To experimentally demonstrate the sensor's excellent selectivity to ammonia, it was exposed to six other different volatile gases at room temperature. It can be seen from Fig. 9 that the dip wavelength shift only occurs when the proposed sensor is exposed to ammonia gas. It is an important prerequisite when developing the proposed sensor for industrial ammonia gas sensing applications.

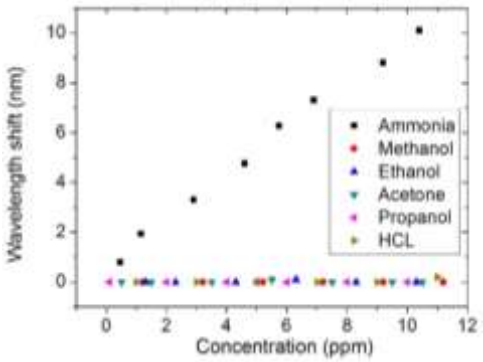


Fig. 9. Selectivity of the proposed sensor to ammonia gas.

IV. Conclusion

In summary, we report an ammonia gas sensor based on a silica gel coated MFC. The change in the refractive index of the silica gel coating induced by the changes in the surrounding ammonia gas results in a spectral shift of the sensor's transmission spectrum. The coating thickness strongly influences the ammonia gas sensitivity. In the experiment, the proposed microfiber coupler based sensor is formed by two weakly fused fiber tapers with 3 μm waist diameter each and 90 nm coating thickness of silica gel. The sensor offers a highest sensitivity of 2.23 nm/ppm, excellent repeatability and selectivity. The response and recovery times are less than 50 and 35 seconds, respectively. This study serves as a prerequisite for further development of the proposed sensor for industrial ammonia gas sensing applications and demonstrates the immense potential for the development of other gas sensors based on a tapered optical fiber coupler coated with sensing material layers.

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