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ABSTRACT

A new type of fiber optic sensor for detection and quantification of ammonia (NH_3) vapors is proposed and experimentally demonstrated. This sensor is based on a spherical silica micro resonator coated with porous silica gel. Whispering gallery modes (WGMs) in the micro resonator are excited by evanescent coupling to a tapered fiber with a 3.3 μm waist diameter. The optical properties of the porous silica layer change when it is exposed to ammonia vapor, leading to a spectral shift of the WGM resonant wavelengths. The sensitivity of the proposed sensor has been tested by exposing it to different low level concentrations of ammonia: 4 ppm,8 ppm,12 ppm and 30 ppm at constant relative humidity (50% RH) and constant temperature (23^0C). The response and recovery times are measured as 100 and 570 seconds respectively.

Keywords: Optical resonator, whispering gallery mode, ammonia sensor, fiber optic sensor

1. INTRODUCTION

Ammonia(NH_3) is a highly toxic and corrosive substance that can be found both naturally and produced by humans in various fertilizers, refrigeration systems, during manufacturing of dyes, drugs, synthetic fibers, etc.[1,2].The lower limit of human NH_3 perception by smell is around 50 ppm[3].Increasing the concentration of ammonia in air causes severe adverse effects in the human respiratory system, eyes and skin. Over the past decade, several techniques for detection of NH_3have been reported based on measurements of electrical current in nano structured metal oxides [4], conducting polymers[5], carbon nanotubes[6] and nano structured graphene [7].Optical fiber based sensors have some unique advantages over their electrical analogues such as remote and real time monitoring, immunity to various sources of disturbance such as electromagnetic interference, radioactivity, and explosive environments. Amongst the optical fiber techniques, sensors based on the whispering gallery modes (WGMs) in spherical microresonators found many applications in the fields of molecular adsorption [7],refractive index[8],temperature [9] and gas sensing[10] due to their ultra-high quality factors, low absorption losses and inexpensive fabrication. WGMs in a spherical microresonator rely on total internal reflection at the microsphere interface. Due to large refractive index contrast between the microsphere and surrounding medium the radiation loss is typically very small, resulting in a very high Q factor. Polymer coated spherical micro resonators have been previously reported for chemical vapor sensing [11]. When such an optical micro resonator is coated with a thin layer of polymer, WGM frequency shift occurs when the polymer undergoes a change in its refractive index or thickness due to the absorption of chemical vapors.

In this paper we propose a new type of fiber optic ammonia vapor sensor based on a microsphere resonator coated with porous silica. Porous silica gels were prepared by acid hydrolysis of Tetraethyl orthosilicate (TEOS).WGMs in the microsphere resonator are excited by evanescent coupling of light using a tapered fiber with a waist diameter of 3.3 μdetailed investigation of the sensor performance has been carried out by exposure of the sensor to low concentrations of ammonia vapor in the gas chamber.

2. EXPERIMENTAL

2.1 Synthesis of porous silica gel

Porous silica gel is typically prepared in laboratory conditions by sol-gel polymerization of tetra orthosilicate under hydrolic conditions using either acids or base catalysis. For our experiments Tetraethyl orthosilicate (TEOS), Ethyl alcohol and sulphuric acid (H_2SO_4) were purchased from Sigma- Aldrich and were used without any further purification. 10 mL of TEOS and 5 mL of ethanol were mixed in a 250 mL measuring flask and kept in a magnetic stirrer for 20 minutes at room temperature. 1.5 mL of H_2SO_4 was poured in to the TEOS solution in the flask under constant stirring. The solution turned to gel form after 3 hours of continuous stirring. The pore size is extremely small and evenly spread in the acid catalyst [12].The individual silica particles cannot be resolved. Hence the gel appears to be transparent.

2.2 Device fabrication and characterization

The microsphere for our experiments was fabricated at the tip of a standard single mode fiber. The cleaved end of the fiber was put inside a fusion splicer (Sumitomo Type-36). A series of electric arc discharges was applied to the cleaved part of the fiber, so that the tip of the fiber was gradually softened and became spherical in shape due to surface tension. Microsphere samples were dipped into the silica gel and pulled out very fast. Coated porous silica microspheres were kept for drying at room temperature for 24 hours. Tapered fiber was fabricated using a customized micro heater brushing technique [13]. A few centimeters of coating length was removed from the fiber before tapering. Then the fiber was placed horizontally using two computer controlled XYZ translational stages pulling the fiber through the micro heater opening. During tapering, translation stages were moved horizontally at the same time fiber was being stretched by the stages. In our experiment the tapered waist diameter is approximately 3.3 micron. The fabricated fiber taper was then fixed on a glass slide at a height of ~5 mm from the slide surface using two drops of UV curable epoxy (Norrland).

2.3 Vapor phase detection

The fabricated device was kept in a chamber of approximately 106 L in volume. For vapor sensing experiment, a certain volume of the analyte was injected into the test chamber by using micro syringe. The concentration of vapors was calculated using following equation. (1) [14]

$$C_{ppm} = \frac{V_{\mu L} \times D_{gmL^{-1}}}{M_{gmol^{-1}} V_{mL}} \times 2.42 \times 10^7 \quad (1)$$

where, C_{ppm} is the required vapor concentration , $V_{\mu L}$ is the volume of the liquid analyte , $D_{gmL^{-1}}$ is the density of the liquid ,V_{mL} is the volume of the rest chamber and $M_{gmol^{-1}}$ is the molecular weight of the liquid analyte. All the subscripts are the corresponding units. The temperature inside the test chamber has been kept constant at 22 °C throughout the experiment.

3. RESULTS AND DISCUSSION

The experimental setup for characterization of the gas sensor consists of a broadband light source (Thorlabs S5FC1005S), polarization controller, optical spectrum analyzer (OSA, Advantest Q8384) and a temperature controlled humidity chamber (ETS 5503). The coated microsphere was mounted in an XYZ nano-positioning stage and then slowly placed in contact with the tapered fiber inside the test chamber. Light from the broadband superluminescent light source (SLD) operating in the wavelength range 1530-1570 nm was launched into the fiber taper and the corresponding transmission spectrum was observed at the taper output by means of the OSA. The wavelength resolution of the OSA was 10 pm. The microsphere was gradually and carefully brought in direct contact with the tapered fiber until the WGM resonances were clearly observed in the transmission spectrum of the fiber taper. The polarization controller was also adjusted manually to achieve maximum light coupling efficiency. Figure 1 (a) illustrates a typical fiber taper transmission spectrum achieved with porous silica coated microsphere. As can be seen from Fig. 1(a), periodic transmission dip can be observed. The value of the free spectral range (F.S.R) determined from the graph (1.9 nm) can be used to estimate the microsphere diameter or its effective refractive index based on the approximate formula [15]:

$$\text{F.S.R} \approx \frac{{\lambda_0}^2}{\pi D n_s} \quad (2)$$

whereλ_0,$n_s$and$D$ are the resonant wavelength, the refractive index of the microsphere and the microsphere diameter, respectively. As the sphere diameter is 282 µm from Fig.1 (b), the refractive index of the porous silica is close to n_s = 1.42 which is a good agreement with the result reported in the previous publication [16].

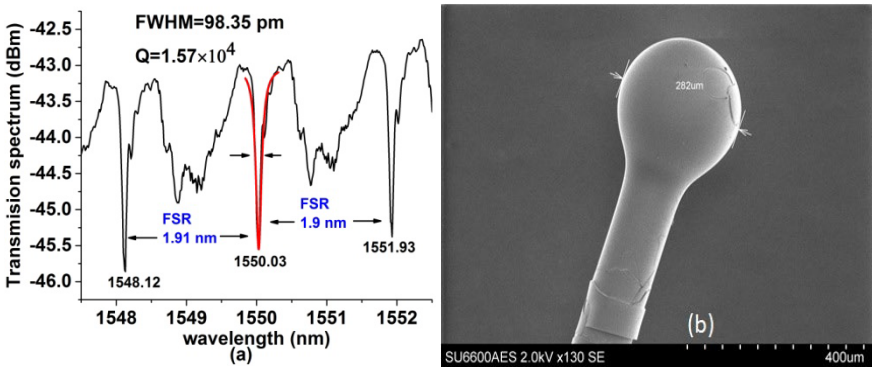
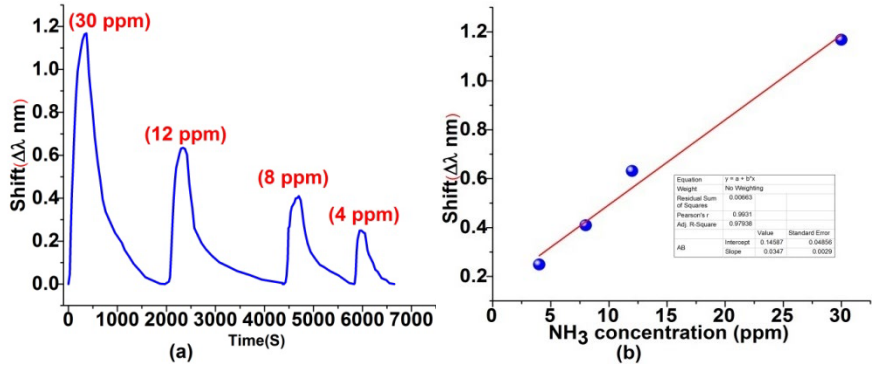


Fig.1. (a) Transmission spectrum recorded with porous silica coated microsphere with a diameter of 282 µm. (b) SEM image of porous silica coated microsphere used in experiment.

To investigate the sensing response of the porous silica coated microsphere toNH_3vapor, small amounts of NH_3 were injected into the gas chamber in sequence to create several low concentrations corresponding to 4 ppm, 8 ppm,12 ppm and 30 ppm of ammonia in air. As shown in Fig. 2(a), the WGM resonant wavelength experiences red shift when the sensor is exposed to NH_3. The main reason behind the shift is a change in the effective refractive index of the silica coating when NH_3 molecules were adsorbed on the surface of the sphere. A higher concentration of NH_3 leads to a larger red shift in the resonance wavelength with a very short response time. Upon turning open the valve of the gas chamber, the resonance wavelength recovers to its initial position. Thus, it can be concluded that the resonator exhibits excellent response and recovery times suitable for NH_3 detection. The maximum shift in the resonance wavelength was then plotted as a function of ammonia concentration as shown in Fig. 2(b).



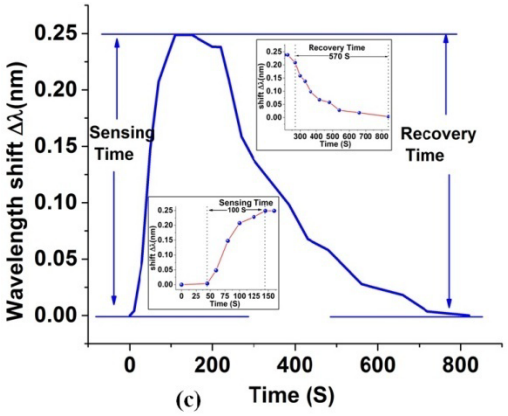


Fig.2. (a) Sensing response of the porous silica coated spherical resonator with different concentration of NH_3 vapors ranging from 30 ppm to 4ppm. (b) Sensor response as a function of NH_3 concentration.(c)Response and recovery time of NH_3 sensor in response to 4 ppm of vapor NH_3

The response and recovery times are two crucial parameters for any gas sensor. The response time is the time taken for a sensor to reach 90% of the total shift in resonance wavelength after exposing to vapors of ammonia inside the chamber, whereas the recovery time is the 90% of the change in wavelength after withdrawing the vapors from the chamber. The response time of the device to 4 ppm of NH_3 was calculated to be approximately 100s, whereas the recovery time was measured to be 570s as shown in Fig 2(c).

The detection limit of the porous silica coated spherical resonator is calculated using method reported in [17]. The *Q*-factor of the 282 µm coated microsphere calculated from the transmitted spectrum was 1.57×10^4 and the full-width half maximum (FWHM) calculated by fitting the resonance dip with Lorentz equation was 98.35 pm at $\lambda = 1550.03$ nm. The detection limit of a 282 µm diameter porous silica coated microsphere is calculated as 57 ppb of ammonia which is 10 times better than that previously reported for a perylenediimide thin film coated gas sensor [14].

4. CONCLUSION

A novel type of ammonia sensor based on a whispering gallery mode microresonator has been proposed and experimentally demonstrated. The proposed sensor offers the advantages of compact size and high sensitivity. Experimental studies revealed excellent performance of the proposed sensor with fast response and recovery times and a detection limit of 57 ppb.

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