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High Sensitivity Sol-Gel Silica Coated Optical Fiber Sensor for Detection of Ammonia in Water

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Abstract: A high sensitivity ammonia sensor based on a tapered small core singlemode fiber (SCSMF) structure for measurement of ammonia concentration in water is reported. Two tapered SCSMF fiber structures with different waist diameters of 23 µm and 13.5 µm are fabricated by using a customized microheater brushing technique. The silica based material prepared by the sol-gel method is used as a coating applied to the surface of the tapered fiber structures. To investigate the influence of the coating thickness on the sensitivity to ammonia in water, silica coatings with different thicknesses (2-pass and 8-pass coatings) are deposited on the surface of the fiber sensor with a waist diameter of 23 µm. Experiments demonstrate that the sensor with a thicker (8-pass) silica coating shows better sensitivity of 0.131 nm/ppm to ammonia compared to that of 0.069 nm/ppm for the thinner silica coating (2-pass). To further improve the sensor sensitivity, the taper waist diameter is reduced. For an 8-pass coating (249nm at the taper waist section) applied to a tapered SCSMF structure based fiber sensor with a reduced waist diameter of 13.5 µm. Experimental results show that the sensitivity to ammonia is significantly improved to 2.47nm/ppm. The best measurement resolution for ammonia concentration in water is estimated to be 4 ppb while the response and recovery times are less than 2 and 5 minutes respectively. The proposed sensor also offers good performance in terms of repeatability and good selectivity for sensing ammonia compared to that of other common ions and organic molecules in water.

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1. Introduction

Ammonia plays a critical role in many applications; it has been widely used in various industrial processes, agricultural activity and in a number of biological systems [1,2]. However, excess ammonia has a toxic effect on the health of plants, animals as well as human beings, and hence it is essential to quantitatively and qualitatively sense the concentration of ammonia in water to prevent environmental pollution. Recently, a number of sensing techniques were proposed to measure ammonia concentration, such as an electro-chemical method [3], metal oxide semiconductor detectors [4], a ratiometric fluorescence sensor [5], and fiber optic based sensors [6–8]. Among these techniques, fiber optic based sensors have been attracting greater attention because of their unique properties, including miniature size, immunity to electromagnetic interference, remote sensing capabilities, and the possibility of operation at room temperature.

Implementing ammonia sensor based on an optical fiber will usually require that some additional coating material is deposited on the fiber surface. By monitoring the changes in optical properties of the fiber coating resulting from the physical or chemical reactions between ammonia and the coating material, the level of ammonia concentration can be detected. A number of optical fiber based ammonia sensors have been reported to date and can be divided into two categories depending on the physical principle of operation. One category of sensors are based on detecting refractive index (RI) changes that result in wavelength shifts or power level changes in the transmission response spectrum of the sensor caused by the reactions between ammonia and coating materials (Type I); the other category of sensors are based on either measurement of absorption or fluorescence of traditional dye indicators (Type II). The coating materials used in Type I sensors are usually porous materials or nanomaterials, such as nano-assembled mesoporous coating of alternate layers of poly(diallyldimethylammonium chloride) (PDDA) and SiO_2 thin films [9,10], ZnO nanostructures [6] and ITO (In_2O_3 + SnO_2 in the ratio 90:10) [7]. The coating materials commonly employed in the Type II sensors involve polyaniline nanofibers [8] or organic dye (such as bromocresol purple (BCP)) immobilized porous silica membranes [11]. Sensors of

Type I often suffer from inadequately low sensitivity at low ammonia gas concentrations (the detection limit is typically in the order of ppm), which may be attributed to the limited sensitivity of the fiber structure to the changes of the coating's RI or the coating material's poor absorption of ammonia. Sensors of Type II show excellent properties both in terms of ammonia gas sensitivity and low detection limit (typically in the order of ppb), but dye indicators do have some limitations such as high cost, limited lifetime, and low tolerance to the presence of ultraviolet light [12].

Numerous studies have been carried out on ammonia sensing in a gaseous environment, but research on ammonia sensing in water is relatively rare. One of the possible reasons is that sensing ammonia in water imposes much higher requirements on the sensor in terms of its stability and repeatability because preserving the coating's properties in water can be a challenging task. Most previously reported optical fiber sensors for ammonia sensing in water have been based on a Type II operating principle. For example, Tao et al. reported an optical fiber probe for ammonia sensing in water by coating a BCP immobilized porous silica membrane and a thin PDMS layer on the surface of a bent optical fiber core. The lowest ammonia detection limit achieved in this work was 5 ppb [13]. Duong et al. proposed a fluorescence based ammonia sensor which features a short response time, high reversibility and long-term stability for a range of ammonia concentrations 1-60 ppm [14]. All of the previously reported sensors above have achieved good ammonia sensitivity in water but they suffer from the limitations of Type II dye based sensors mentioned previously. There is a previously reported sensor based on a Type I operating principle [10], which reported a SnO_2 thin film coated fiber sensor for detecting ammonia in water, but the sensor has a limited resolution of only 2 ppm. In this work, we describe a sensor of Type I to detect ammonia concentration in water, which does not suffer from the limitations of Type II sensors and addresses the challenge of achieving high sensitivity (sensitivity is improved by three orders of magnitude compared with [10]).

SMS (single mode-multimode-single mode) fiber structures are commonly used as the basis for a variety of sensor types, with chemical etching of the multimode fiber required in some applications. In our previous reports, we have proved that a small core singlemode fiber (SCSMF) is a good candidate to replace the multimode fiber section in an SMS fiber structure, with the advantage that chemical etching is not required [15–17]. Most recently, we reported a tapered SCSMF structure, which has a very high RI sensitivity of 19212.5 nm/RIU (RI unit) in the RI range from 1.4304 to 1.4320 [18]. In this work, we propose and demonstrate a highly sensitive optical fiber sensor based on a tapered SCSMF structure. The sensor's operation is based on the Type I principle for the measurement of ammonia concentration in water, without the need for coating with dye materials. The proposed sensing structure was obtained by coating a thin layer of sol-gel silica on the tapered SCSMF structure surface. Compared with other coating nanomaterials, silica shows better adhesion to the fiber surface because both the optical fiber sensor and sol-gel silica are made of silica material.

Although the effect of adsorption of ammonia on the silica surface is well known [19,20], to the best of our knowledge there are no reports to date of the use of this effect in fiber optic sensors of Type I (silica is commonly used in sensors of Type II, but it is not used as the sensing materials). In this letter we experimentally demonstrate a novel sensor for detecting ammonia concentration in water fabricated by tapering of an SCSMF structure waist down to 13.5 μm and subsequently applying a silica coating upon its surface.

Adsorption of ammonia by the silica material results in a change of the silica coating RI which in turn leads to the spectral shift of the transmission response of the fiber sensor. Thus ammonia concentration can be measured by detecting the variations of the sensor's spectral response assuming a suitable calibration has taken place.

2. Experimental setup and sensor fabrication

In this experiment, two tapered SCSMF structures with tapered waist diameters of 23.0 µm (denoted as S-23) and 13.5 µm (denoted as S-13.5) were fabricated by using a customized microheater brushing technique [21]

A silica sol solution for the coating layer was prepared as follows: 1) 10 ml of hydrolyzing tetraethylorthosilicate (TEOS) was mixed with 5 ml ethanol using magnetic stirring for 20 min at room temperature; 2) then 1 ml 0.1 mol/L HCl solution was added into the mixture followed with further stirring for 240 min; 3) the obtained silica sol solution was sealed in a small bottle and stored in a refrigerator during the experimental trials. Each sensor sample was fabricated by applying a thin layer of silica on the tapered fiber surface by passing the tapered SCSMF section through a drop of the silica sol solution using a motor controlled translation stage. A single pass of the silica drop from one side of the fiber to the other side is defined as a one-pass coating. By repeating the one pass coating process, different silica coating thicknesses can be realized. It should be noted that after each pass the coating was left to dry for ten minutes before the next coating layer was applied. When the desired number of coating passes were completed, the fiber sensor was cured firstly at room temperature for 24 hours and then heated at 120°C for two hours, followed by an additional 24 hour period of drying at room temperature. Before the ammonia test, the coated sensors were immersed in water overnight to eliminate the influence of water penetrating into the silica coating on the sensor performance. It is noted that all water used in this experiment is deionized water. Various ammonia concentrations in water were prepared by mixing "ammonia solution 0.88" with deionized water.

Figure 1(a) illustrates a schematic diagram of the silica-coated ammonia sensor and Fig. 1(b) shows a schematic diagram of the test system for ammonia sensing in water. The functionalized fiber ammonia sensor was placed in a PDMS mould with a narrow channel and the water/ammonia sample was pumped through the channel by a peristaltic pump at a speed of 20 r/min. This enabled the water/ammonia sample to flow slowly through the volume surrounding the sensor. Light from a broadband light source (Thorlabs S5FC1005S) is launched into the tapered SCSMF structure and the transmitted light is measured by an optical spectrum analyzer (OSA) (Agilent 86142B). All the tests were conducted at room temperature.
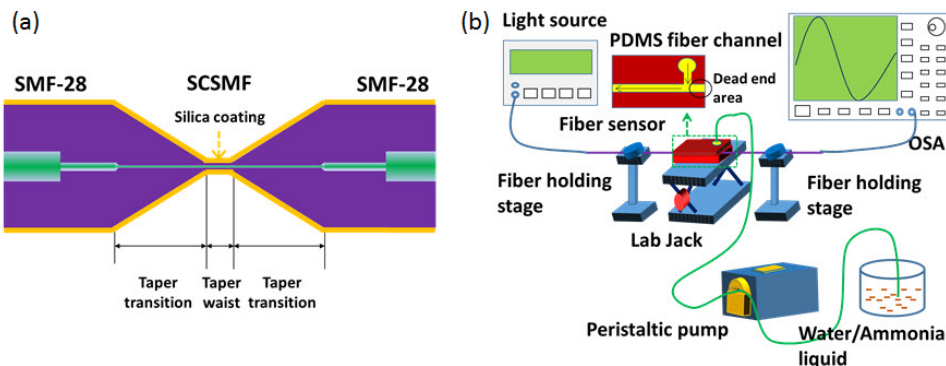

Fig. 1. Schematic diagram of: (a) Tapered SCSMF structure and (b) Experimental setup for ammonia sensing in water.

3. Results and discussion

Figure 2 shows the measured spectral shift for the S-23 taper with two different coating thicknesses (2-pass and 8-pass coating) for various ammonia concentrations in water. In our experiment, the sensor's sensitivity S is defined as $S = \Delta\lambda / C$, where $\Delta\lambda$ represents the

corresponding spectral wavelength shift under different ammonia concentrations and C is the ammonia concentration in water. It is noted that in this study, the spectral shift is determined as the shift of the 3 dB mean wavelength of the selected spectral dip in the SCSMF transmission spectrum. From Fig. 2 it can be seen that as the ammonia concentration in water increases, the wavelength of the spectral dip shifts to a longer wavelength. Sensors with 2-pass and 8-pass coatings have sensitivities of 0.069 nm/ppm and 0.131 nm/ppm respectively at an ammonia concentration of 2.6 ppm, while at a concentration of 65 ppm, the sensitivities are 0.018 nm/ppm and 0.059 nm/ppm respectively. The results indicate sensor with a thicker sol-gel coating (8-pass coating in Fig. 2) has a higher sensitivity in the whole range of the tested ammonia concentrations. For both silica coating thicknesses, the sensitivity of the ammonia sensor decreases as the ammonia concentration increases.
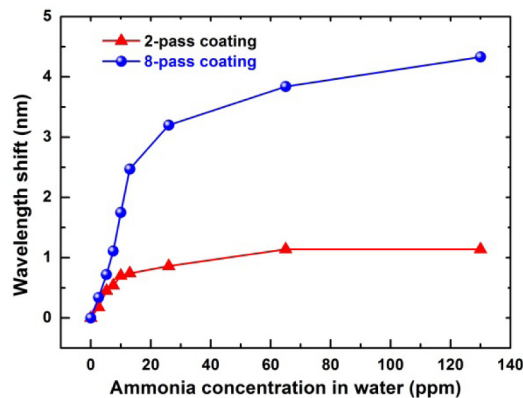

Fig. 2. Measured spectral dip shift vs. ammonia concentration in water for S-23 with different coatings.

Decreasing the tapered waist diameter is a common strategy used in tapered fiber sensor to improve sensitivity. Thus in this work in we investigated whether an improvement in the sensitivity could be achieved by tapering the SCSMF section to a smaller diameter of 13.5 µm with 8-pass coating by the silica sol-gel. Figure 3(a) shows the measured spectral responses for the S-13.5 sensor at different ammonia concentrations in water and Fig. 3(b) shows the dependency of the measured wavelength shift vs. ammonia concentration. As one can see from Fig. 3(b), compared to the sensor S-23, the alternative sensor S-13.5 has significantly higher sensitivity. When the ammonia concentration is 2.6 ppm, the measured dip wavelength shift with respect to its position corresponding to pure water is 6.43 nm compared to that of 0.34 nm for the previous sensor shown in Fig. 2. As the ammonia concentration increases, the dip wavelength shifts to longer wavelength monotonically. However the shift rate decreases as ammonia concentration increases, which indicates that the sensor has higher sensitivity as well as better resolution for lower ammonia concentrations. The sensitivity is estimated to be 2.47nm/ppm at 2.6 ppm and 0.67nm/ppm at 65 ppm. Assuming the OSA has a wavelength resolution of 0.01 nm, the best resolution of the developed sensor at 2.6 ppm ammonia concentration could be as low as 4 ppb. It is worth pointing out that while reducing the tapered waist diameter of such a fiber sensor even more might result in a higher sensitivity, a tapered fiber with a smaller waist diameter is more fragile compared to that with a larger waist diameter, which could limit the sensor stability, depending on the packaging technology used in an actual application.
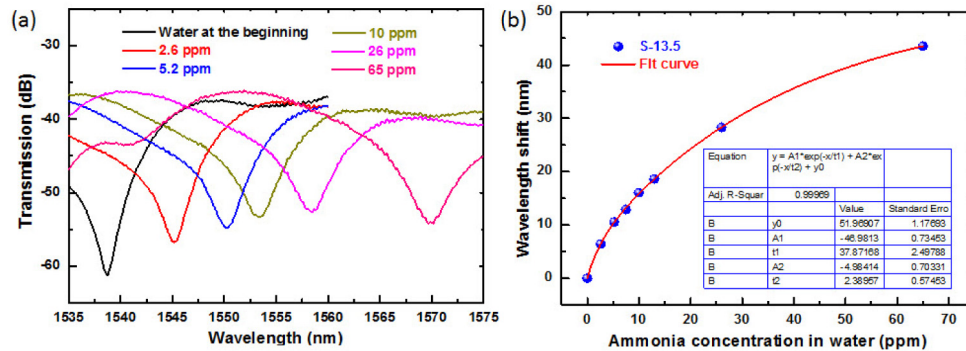
Fig. 3. (a) Measured spectral response of S-13.5 at different ammonia concentrations in water; (b) Measured spectral wavelength shift vs. ammonia concentration in water (varies from 2.6 ppm to 65 ppm) for S-13.5 with 8-pass coating; measured data fitted with nonlinear function parameters of which are listed in the inset table.

The response and recovery times are illustrated for a range of ammonia concentrations in Fig. 4. The response time is defined as the time that takes the sensor to reach 90% of its full response and the recovery time as the time to fall down to 10% of the full response. The sensor's response time is estimated to be less than 2 minutes, while the recovery time is estimated to be less than 5 minutes. It should be noted that in our experiment the water/ammonia liquid sample is being constantly pumped through the PDMS channel to avoid mechanical instabilities of the fiber sensor associated with replacement of the liquid sample. It is estimated that it takes about 30 s to fully replace the liquid sample within the PDMS channel of the adopted geometry and pumping speed. Most importantly, there is a "dead end" area (shown in Fig. 1 (b)) within the channel where liquid is never replaced but continuously dissolving into the new input water/ammonia liquid sample every time we replace it. Hence, it takes a longer time to eliminate the difference between the former liquid sample and the new one in the dead end of the channel and to equalize the ammonia concentration. Due to these shortcomings of our setup, the actual response and recovery times may well be even shorter.
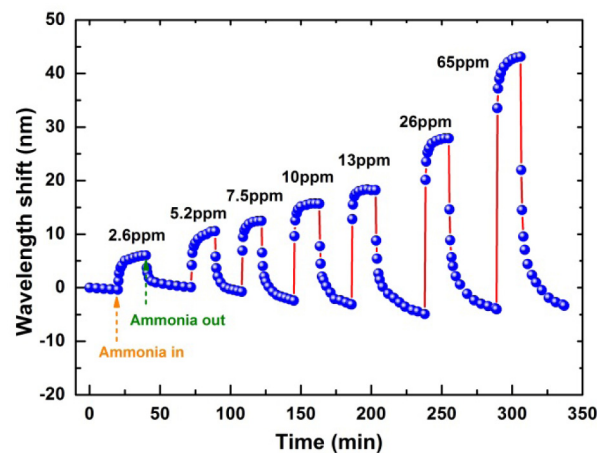

Fig. 4. Sensor's response and recovery at different ammonia concentrations.

The morphology of the silica coating is also investigated using a scanning electron microscope (SEM) using a separate sample but with same fabrication parameters. The SEM images of a fiber sensorwith a waist diameter of 13.5 μm coated with silica coating are shown in Fig. 5. One can see from the image that the silica coating is smooth at the taper waist section, while the taper transition section is mostly smooth but with some small cracks (as

shown in the inset SEM images Fig. 5(b)). From the cross-section SEM image, the coating thickness at the taper waist is estimated to be 249 nm as shown in the inset SEM image Fig. 5(a). It is noted that the position of the spectral dip in pure water after each ammonia sample measurement gradually moved to a shorter wavelength. One possible explanation for this is that the silica coating is being gradually removed from the fiber surface due to the cracks and non-ideal bonding to the fiber surface (as shown in Fig. 5) after long term immersion in the ammonia/water solution. In addition, the continuous flow of the liquid may also accelerate the separation of silica from the fiber surface. Furthermore, silica coating seems easier to be removed by a flow of the liquid sample from the fiber section with lager diameter, containing the cracks shown in Fig. 5(b). A possible solution to the problem of coating deterioration is the application of an additional protection layer over the silica coating, such as a thin layer of PDMS, which is known to perform well in water for the protection of both the silica coating and the dye [11].
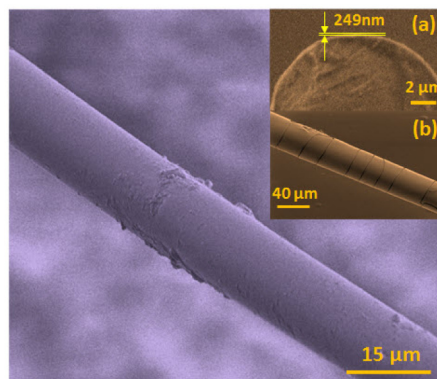

Fig. 5. Silica coating morphology at the taper waist. The inset SEM images show (a) cross section at the taper waist; (b) taper transition section.

The reproducibility of measurements for the ammonia sensor at low and high concentrations has also been investigated and the experimental results are shown in Fig. 6. The dip wavelength shifts are also summarized in Table 1. The reproducibility measurements were performed 24 hours later following the experiments with various ammonia concentrations (we refer to the previous experiment as the "1st day test" while to the reproducibility measurement as the "2nd day test"). Figure 6 shows that our sensor exhibits good reproducibility. However it is worth noting that during the "2nd day test", when the sensor was tested three times within a short time frame (30 minutes between the tests), the wavelength shift (and hence sensitivity) decreases slightly after each consequent test for both low and high ammonia concentrations. This might be due to the fact that some residual ammonia molecules are not fully desorbed from the silica coating during the 30 min gap between these tests.
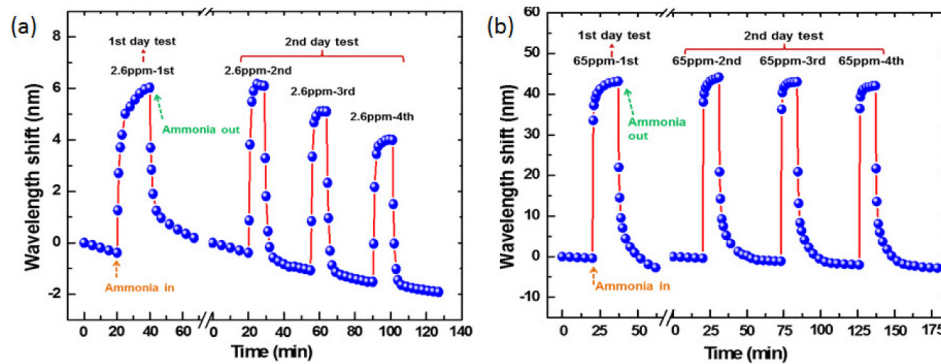
Fig. 6. Sensor's response illustrating reversibility and repeatability of measurements for S-13.5 at low and high ammonia concentrations: (a) 2.6 ppm; (b) 65 ppm.

Table 1. Wavelength shift of the spectral dip for the S-13.5 sensor for a series of repeat tests at 2.6 ppm and 65 ppm ammonia concentrations in water.

	1-st test (nm)	2nd test (nm)	3rd test (nm)	4th test (nm)
2.6 ppm	6.43	6.51	6.17	5.47
65 ppm	43.53	44.56	44.14	44.09

A key parameter for an ammonia sensor is its cross sensitivity to other chemical compounds. Thus the sensor's sensitivity to some other common ions in water and some organic molecules was also investigated. The presence of methanol, ethanol, $CaCl_2$, NaCl, $Al_2(SO_4)_3$ and NaH_2PO_4 in water was tested separately, and the experimental results are shown in Fig. 7. It is clear that silica coating shows very low sensitivity to those ions and molecules in comparison with that to ammonia, which indicates that our sensor exhibits good selectivity to ammonia.
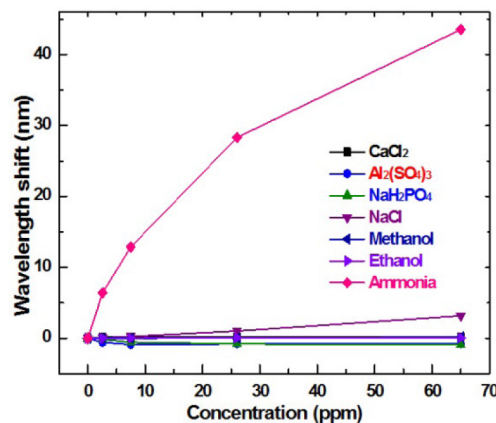

Fig. 7. Sensor's sensitivity to a range of ions and molecules including methanol, ethanol, $CaCl_2$, NaCl, $Al_2(SO_4)_3$, NaH_2PO_4 and ammonia in water.

4. Conclusion

In conclusion, a novel ammonia sensor is proposed and experimentally investigated based on a silica-coated tapered SCSMF fiber structure. Two tapered SCSMF fiber structures with different taper waist diameters of 13.5 μm and 23 μm were fabricated using the microheater brushing technique. Silica sol-gel was prepared and coated on the fiber surface as a sensing layer for detecting ammonia concentration in water. The influence of the coating thickness on

the sensitivity to ammonia in water is investigated by characterizing two sensors with different coating thickness (2-pass and 8-pass coatings). Experiments demonstrate that the sensor with a thicker (8-pass) silica coating shows better sensitivity of 0.131 nm/ppm to ammonia compared to 0.069 nm/ppm for a thinner (2-pass) silica coating. A sensor with improved sensitivity was prepared by tapering the SCSMF to a smaller waist diameter of 13.5 μm. The experimental results confirm that the sensor with an 8-pass coating offers an improved sensitivity of 2.47 nm/ppm compared to that of 0.131 nm/ppm for the sensor with a 23 μm waist diameter. The coating thickness (8-pass) was independently estimated using SEM images as 249 nm at the taper waist section for the sensor with a 13.5μm waist diameter. The best resolution of the ammonia sensor is estimated to be as low as 4 ppb while the response and recovery times are less than 2 and 5 minutes respectively. The best resolution of the ammonia sensor is estimated as low as 4 ppb while the response and recovery times are less than 2 and 5 minutes respectively. In addition, the sensor shows good repeatability and good selectivity to ammonia amongst a range of common ions in water and some organic molecules.

Acknowledgment