Short Communication

Performance Evaluations of Ammonia Sensors Using Cladding Modified Single-Mode Optical Fiber Coated with Polyaniline Nanofibers

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Abstract

In this paper, we developed a cladding modified optical fiber to detect low concentrations of ammonia (NH_3). The Modification is coating with polyaniline (PANI) nanofibers. By using single mode optical fiber (SMF), two sensors are fabricated. The first one is etched with the chemical agent which is hydrofluoric acid (HF), and the other is tapered with a glass processing workstation so that the waist diameters of 15 µm for both modified sensors. Modified fibers are spray coated. The modification done on SMFs considerably enhances the interaction between them. The proposed modification is considerably enhancing how the evanescent field and the (PANI) sensing layer interact with each other. The modified SMF sensors are subjected to NH_3 with different concentrations within the visible wavelength range. The modified SMF and the nanostructured PANI films pattern results in a highly sensitive ammonia sensor at room temperature. The tapered SMF coated with PANI works better compared with the etched SMF. The results show that the response equals 89s, the recovery times equal 433s, and the sensitivity equals 139.1%. The modified fiber sensors have a limit of detection (LOD) of 0.0034% (34 ppm).

Keywords: *Ammonia sensor, Modified SMF sensor, Etched sensor tapered sensor, Polyaniline nanofiber, Visible band sensors.*

1. INTRODUCTION

NH_3 is extensively used in several applications like chemical industries [1-4]. NH_3 is characterized to be colorless with apungent smell [1, 5]. Largely, exposure to ammonia in the air could cause intense poisoning or life-endangering conditions. Consequently, for the safety of environments, there is an urgent necessity to develop -highly sensitive and reliable sensors as a key matter to detecting NH_3 leakages. A leak of NH_3 gas may cause disasters [5-9].

Cladding modified fibers are combined with h nanomaterials such as conductive polymers (CPs) so that CPs areused as a sensing layer [1, 10-13]. The interaction of NH3 with CPs varies in evanescent fields [14-15]. CPs, for instance, polyaniline (PANI) is well studied in the literature. PANI is known to perform at room temperature with high sensitivity and good response time [11, 16-19]. PANI shows variations in the electrical conductivity and optical absorption on exposure to NH_3 therefore it is proposed for sensing NH_3. The state of oxidation and protonation alters the polymer's properties. Emeraldine salt (ES) PANI (acid or doped form) will be converted into non-conducting emeraldine base (EB) PANI (deprotonated or dedoped) as exposed to NH_3 [11]. It is noted this is reversible switching. This change in absorbance is the basis of PANI based optical sensors. There are many researchers studied the utilization of electrical sensors coated with PANI. In contrast, the utilization of optical fiber sensors for NH_3 detection employing PANI has not been well established [11].

In this paper, we propose PANI nanostructured thin film coated modified SMF sensors for ammonia sensing applications. Two modified sensing platforms etched and tapered SMF are fabricated. The fabricated sensors were subjected to NH_3 and investigated at room temperature in the visible wavelengths range. The proposed modification strongly enhances the sensitivity of optical fiber sensors that can operate at room temperature. In order to have a quick and highly sensitive response, the fiber diameter is chosen to be around 15µm, which is extremely small. However, such a small fiber dimension will be challenging in terms of handling as it is highly vulnerable to surrounding perturbations. PANI nanostructured thin film that coats modified SMF is not fully investigated in visible and IR wavelengths ranges.

2. SENSOR FABRICATION AND INVESTIGATION SETUP

In the experimental work, we utilize typical SMF-28 silica fiber (Lucent All-Wave Fiber) for the fabrication of sensing platforms. The sensing platforms are intended for NH_3 monitoring at room temperature. The SMF-28 silica fiber has a core diameter of 9 µm and a cladding diameter equals 125 µm. Two modification processes on the optical fibers were performed. The modifications are the etching and tapering of optical fibers. With the aid of a stripper, the plastic jacket enclosing section of the SMF was removed mechanically. The sensing platform is made from a 1 m length of SMF. The SMF etching was performed using 48% hydrofluoric acid (HF) from Sigma Aldrich. The author in [11] states platform fabrication and preparation. Reduction of the fiber cladding is the purpose of the etching process however, the dimension of the core used in the platform remains without change. The SMF sensing platform was etched so that the fiber diameter equals 15 µm. Thus, the core becomes closer to the surrounding environment. Tapering is a critical portion of the work. We used the Vytran glass processing system workstation (GPX-3000, USA) to fabricate the tapered fiber. The way in which the machine works is based on the heating section of the SMF and pulling in the opposite directions. Tapered SMF was fabricated with parameters up-taper of 2 mm, down-taper of 2mm, waist-length of 10 mm, and waist diameter of 15 µm. CCD camera of the Vytran workstation was used to verify these dimensions. The tapering process extends and shortens the core and cladding dimension of the SMF. Therefore, the ratio of the core to the cladding of the tapered fiber remains unchanged.

2.1. Deposition of PANI on Modified SMF

PANI nanofiber is used to coat the modified SMF for the detection of NH_3 with different concentrations. The principle of polymerization is defined as the preparation and synthesis of emeraldine base PANI nanofiber [11, 20]. PANI solution was prepared by dissolving a 15 mg camphor sulfonic acid (CSA) (Sigma Aldrich) and a 15 mg PANI powder in 8 ml of chloroform as explained by the authors in [11]. The resultant solution has a green color with 3.75 mg/ml concentrations. By using a hotplate, the glass substrates and optical fibers are heated up to 50˚C for half an hour before the spray deposition of PANI. The objective is to boost the binding of the formation of uniform thin films of the nanomaterial. Modified SMF in addition to glass substrates are coated by PANI and then dried for 60 minutes at 25 C. As in [11], the deposition process was carried out under a fume hood. The surface roughness of the etched SMF as a result of the etching process improves the binding of the sensing layer on the surface of the SMF and increases the surface to volume ratio allowing strong interaction with the gas.

2.2. Microcharacterization of PANI Nanostructures

Scanning Electron Microscopy (SEM) is performed to observe the morphology of the PANI nanostructures deposited on the SMF and glass slide as shown in Fig. 1(a and b). Fig. 1(a) was reported by authors in [11] and depicts the sprayed PANI nanofibers on the glass slide. The deposited non-uniform PANI nanofibers agglomerate to form a cluster. As measured, the typical lengths and diameters of PANI nanofiber are approximately 2.5-3.5 µm and around 180 – 200 nm, respectively. The average thickness of the PANI thin film is approximately 400 nm. The average roughness of the surface is 228.2 nm as measured by (AFM) atomic force microscopy reported by authors in [11] and shown in Fig. 1(c). Increased surface roughness affects the sensing performance as it enhances the sensitivity of the sensor. This is because of its high surface area that boosts the interaction between the sensing layer and gas molecules [11].

Description of Gas Sensing Experimental Setup

Fig. 2 depicts the experimental setup used to study the optical response and performance of the modified SMF sensors in the detection of NH_3 with different concentrations.

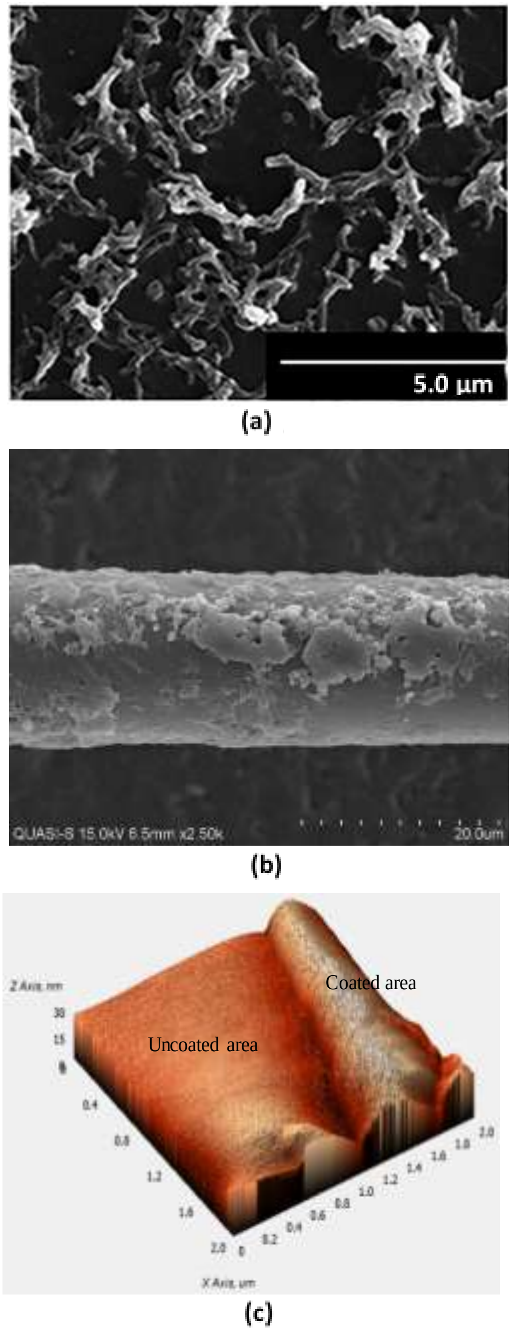

Figure 1. SEM images of (a) PANI nanofibers on glass, (b) etched-tapered SMF transducer coated with PANI nanofibers and (c) 3D AFM image of uncoated and PANI coated areas on a glass substrate.

The setup is used to analyze the modified SMF platform and benchmark it within the visible wavelength ranges. The SMF sensor is positioned inside a gas chamber as seen in Fig. 2. The chamber has an inlet channel and outlet channel in addition to FC/PC linking adapters in order to match the sensors. A tungsten-halogen lamp (Ocean Optics HL2000) light source is linked to the end of the sensor. The next end is linked to a detection system spectrophotometer. The responses of the sensor from the spectrometer were recorded and measured by using spectra suite software. A calibration system (AALBORG) is used to automatically change the concentrations and their purge time. Synthetic air was used as a reference gas in the investigation. Mass flow control (MFCs) were used to purge NH_3 with pure 99% synthetic air into the chamber. The rate of gas flow is fixed at 200 sccm. The sensitivity and dynamic response of the sensors are studied under different NH_3 concentrations. For 8 minutes, each concentration cycle is purged into the chamber. The air regeneration is implemented by purging air into the chamber for 15 minutes.

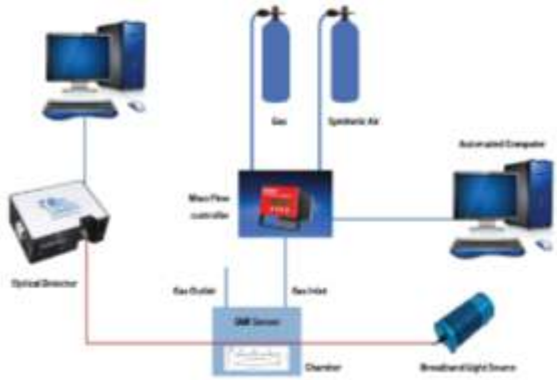

Figure 2. *Investigation experimental setup of the modified SMF sensors coated with PANI thin films in detecting NH_3.*

3. RESULTS AND DISCUSSION

Various concentrations of NH_3 gas are used to test the PANI coated SMF modified sensors for both tapered and etched platforms. The testing is performed at room temperature and within the visible range (600 – 750 nm). The measured absorbance against wavelengths of tapered sensors is shown in Fig. 3. The absorbance of the tapered sensors increases as the increase of concentration. However, the spectral response of the tapered sensor is better compared to the etched one at the same concentration changes. This behavior is attributed to the weak interaction between the evanescent field of the etched only sensor and the PANI sensing layer to produce a strong absorbance change. The highest absorbance change is observed by the tapered sensor. The SMF modification enhances the evanescent field so that the field may detect changes in the emeraldine base form of PANI nanofibers. Therefore, the light intensity passing along the SMF is affected due to the rise in absorbance.

Generally, a substantial rise in absorbance is experienced when the concentrations increased for the two modified sensors. The results show that the PANI sensing layer is darker as exposed to ammonia and absorbance increases. This behavior is due to the deprotonation of the green-colored doped PANI emeraldine salt (PANI-ES) to dark blue colored dedoped PANI emeraldine base (PANI-EB) when interacts with the gas molecules. There was a rise in absorbance accompanied this change [16]. For more details, one can refer to reference [1] as it includes clarification of the NH_3 detection method by PANI coated optical fiber.

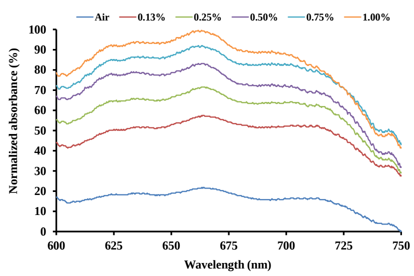

Figure 3. *Tapered SMF sensors absorbance spectrum in detecting NH_3*

Fig.4 shows the dynamic responses of the modified SMF sensors. For the two types of SMF sensors, an increase in the optical response is experienced due to the rise of NH_3 concentrations. Precisely, the response magnitude of the tapered SMF sensor is superior to the etched one. For example, when both are subjected to 1% NH_3, the tapered optical response increases to 100%, while the etched SMF sensor's response increases only to 67.5%. Similar behavior is noticed at lower concentrations. In addition, Fig. 4 shows that the overall response time is lessened when NH_3 concentrations purged are increased for the two types of SMF modifications. On the contrary, the overall recovery time is decreased for the two kinds of modified SMF sensors as NH_3 concentrations are increased. The recovery times and response of the sensors depend on the type of SMF modification and purged gas concentrations. For instance, the response time of the tapered SMF sensor is found to be 93 s at 0.125% and decreased to 78 s when exposed to 1% NH_3 concentrations.

Furthermore, etched only SMF sensor exhibits a response time of 108 s at 0.125% and 89 s at 1% NH_3 concentrations. The tapered fiber shows a faster response. Considering all NH_3 concentrations, the average response time is found to be 89 s for tapered and 102 s for etched SMF sensors, and the recovery times are 433 s and 369s, respectively. The recovery time of the modified sensors is slower, and this is one of the drawbacks of sensors based on polymer [11]. It is likely because of the sensing layer and gas molecules' interaction nature. When the gas is purged into the customized chamber, the molecules of the gas are adsorbed on the sensing layer and therefore, altering the evanescent field intensity. Ref [11] stated that in the period of desorption, the gas molecules need additional energy to leave the sensing layer. This causes the recovery time of the sensors to be increased.

Operating the sensor at room temperature is an important factor that causes the recovery time to be extended. The sensor recovery performance enhances if the operating temperature increases. However, at high temperatures, it is known that PANI conducting polymer changes its structure.

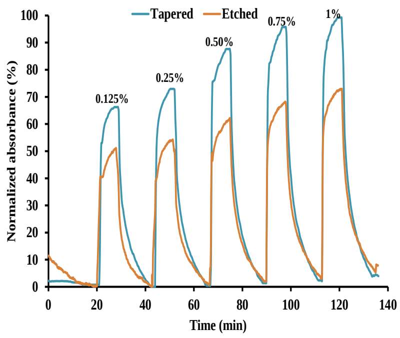

Figure 4. *Modified SMF sensors dynamic response in detecting NH_3 in within visible wavelengths range.*

As compared to the tapered MMF sensor reported in [1], the SMF sensors demonstrate a better response. The MMF sensor exhibited a response time of 136.2 s. SMF sensors used in this work show less recovery time than that of the MMF sensor mentioned in [1] which is 583.8 s.

The practical limit of detection (LOD) of the modified SMF sensor is 0.04 % as shown in Fig. 5. The repeatability and the response of the modified sensors at LOD are investigated in the visible wavelengths range. The absorbance response of tapered sensors is still better than the absorbance response exhibited by the etched one. However, the tapered SMF sensor demonstrates a stronger and quicker response at 0.04% concentrations. The concentration of 0.04% is LOD. It is chosen due to the practical limitation of the gas system used in the experiments. The LOD of the SMF tapered sensor was calculated to be 0.0034%, which is equivalent to 34 ppm. A brief comparison of the developed SMF sensors used in this research in addition to the MMF tapered used in [1] is summarized in Table1.

Table 1. *Modified optical fiber NH_3 sensors performance parameters.*

	Sensor Type	Response time (s)	Recovery time (s)	Sensitivity (%)	Exprimental LOD(%)
1	Etched SMF	102	369	68.5	0.04
2	Tapered SMF	89	433	139.1	0.04
3	Tapered MMF [1]	136.2	583.8	---	0.125

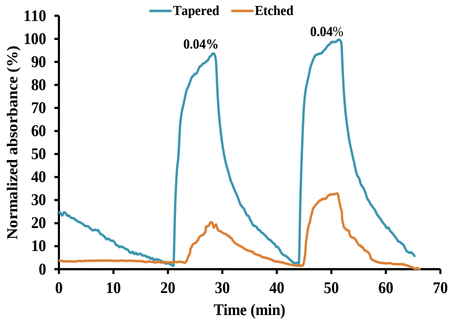

Figure 5. *Modified SMF sensorsLimit of detection and repeatability characteristics in detecting NH_3 within the visible wavelengths range.*

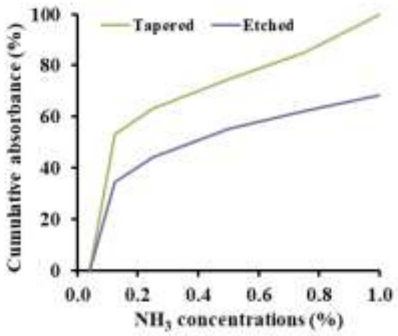

Figure 6. *Modified SMF sensors normalized cumulative absorbance change in detecting NH_3 within visible wavelengths range.*

Fig. 6 shows normalized cumulative absorbance of modified optical fibers subjected to NH_3. Cumulative absorbance is proportional to the increase in NH_3 concentration. However, tapered SMF sensors show the best response. Normalized cumulative absorbance for the tapered and etched sensors are found to be 68% and 100%, respectively, when they are subjected to 1% NH_3 concentrations. The sensitivity (S) is defined as $S = \Delta R/\Delta C$ where ΔR represents sensor response change when exposed to the gas and synthetic air and ΔC represents the gas concentration change as a percentage. The average sensitivity of all concentrations is 139.1% for tapered and 68.5% for etched sensors.

4. CONCLUSION

In this paper, it is successfully proposed and verified modified SMF transducing platforms to sense NH_3 gas at room temperature. The sensor is easy to manufacture, low-cost and responsive. Etching and tapering are the modification processes performed on the SMFs. The modified sensors are investigated at the visible wavelength range (600 – 750 nm). The experiments show that the PANI coated modified optical fiber sensors' absorbance increases as the increase of NH_3 concentration. It is noted that the sensing performance depends on the modification mechanism performed during the fabrication of SMF. The tapered SMF shows a better response than the etched fibers in the detection of NH_3 gas. As a result, the tapered SMF sensor is higher sensitivity and better response than the etched one. This suggests its promising applications such as in environmental monitoring, chemical industries, and remote sensing. In particular, the implementation of the modified SMF sensors makes available easy incorporation with the current optical fiber communication systems.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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