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Development of PPy-PVS optical fiber Ammonia sensor

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In the present investigation we have developed the intensity modulated fiber optic PPy-PVS ammonia sensor, which can be used for the detection of ammonia in the exhaled breath of the patients of liver and kidney disorder. The designing of the sensor is based on the modified cladding technique. Ammonia sensitive layer of the polypyrrole (PPy) doped with different organic and inorganic acids synthesized at room temperature by oxidative chemical polymerization can be acts as a modified cladding. We have synthesized PPy-PVS film with optimized process parameters on sensing probe. Interaction of ammonia with PPy-PVS coated sensing probe changes the optical power at the detector. The effect of probe length, wavelength and power of the source on the sensor response has been investigated. This sensor shows almost stable and repeatable response up to 32 days.

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Keywords: Ammonia sensor, Optical fiber, Modified cladding, Polypyrrole film

1. Introduction

Recently sensor technology represents one of the emerging areas of physics, electronics and biotechnology and hence has been considered as a highly potential field of scientific research. However, biosensors and gas sensor have got vital importance in clinical and biomedical applications [1]. It has been reported that many volatile organic compounds are present in exhaled breath of human being [2, 3]. However, ammonia is also a natural product of human body. It is excreted from the body in the form of urea and ammonium salts in urine. Measuring breath ammonia level (up to 2-3ppm) is a non invasive way for the diagnosis of certain end stage diseases [4]. Research on many breath analyzers are found in the literature [5,6]. Among these, fiber optic ammonia sensor (for measuring breath ammonia level) became a fast diagnostic tool for patients with disturbed urea balance e.g. due to the kidney disorder or end stage liver disease or ulcers caused by Helicobacter pylori bacterial stomach infection [7-11].

In the recent years, the use of optical fibers in the designing and development of fiber optic biosensors and gas sensors has received considerable interest over traditional sensors for the detection of chemical, biochemical, biomedical and gaseous analytes. Excellent light delivery, long interaction length, low cost and ability not only to excite the target molecules but also to capture the emitted light from the targets are the main points in favor of the use of optical fibers in optical biosensors. Optical biosensors are non-conducting, immune to electromagnetic interference and intrinsically safe for patients. Optical fiber biosensors can be used in combination with different types of spectroscopic technique, e.g. absorption, fluorescence, phosphorescence, surface plasmon resonance etc [12] .

In the present investigation, the development of intensity modulated intrinsic fiber optic ammonia sensor is presented which is inexpensive and can be used for the detection of ammonia in exhaled breath. The principle of this sensor is based on the change of optical power or optical intensity induced within modified sensing region of multimode optical fiber. Use of conducting polymers (PPy, PANI etc) as a sensitive layer (modified cladding) for the development of optical fiber sensors have been reported in the literature [13-15]. However, still extensive research has to be done in this area to enhance the sensitivity and response time of the optical fiber sensors.

For the designing and development of fiber optic ammonia sensor, the configuration of the sensor is created on the fiber itself, using the cladding modification methodology. In a small section of an optical fiber, the original passive cladding is replaced by a sensitive cladding of polypyrrole thin film (coating). Recently, PPy has been found to be the best sensing material for various organic vapors and hazardous gases [16]. It has a good conductivity, good thermal stability and shows changes in its resistivity on exposure to different gases and humidity [7, 17-19].

The sensing mechanism is based on the interaction between the light transmitted in the optical fiber with an external chemical perturbation in the modified cladding region which results in the intensity modulation. The interaction between the evanescent field in the cladding and external perturbation, results in the attenuation of the guided light in the fiber core through absorption and fluorescence [17, 20-27]. The light transmitted through the optical fiber with total internal reflection only when angle of incidence is greater than critical angle and refractive index of the core is greater than refractive index of cladding. The total internal reflection condition would no longer exist in the modified region, where the modified cladding has higher refractive index than the core. However, as the modified cladding is very thin and air medium acts as a second layer of the cladding (Fig. 1), a

part of light is refracted and other part of the light is reflected back into the core. Thus the absorption in the modified cladding in presence of evanescent field in sensing region produces the intensity modulation according to the analyte present in the sensing region [28].

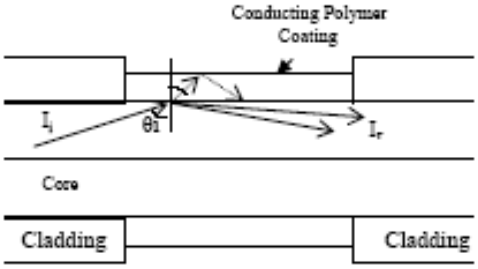

Fig. 1. Diagram showing geometric ray optics through sensing region.

In the present investigation the plastic (PMMA) multimode optical fiber has been used to prepare sensing probe by replacing original cladding with polypyrrole film on certain portion of fiber. The optimization of various process parameters for the synthesis of PPy-PVS films on PMMA substrate has been carried out in the present work. Ammonia sensitive PPy–PVS film was synthesized at room temperature with (in situ-polymerization) optimized process parameters which provide the optimal surface morphology to maximize the gas polymer interaction. This film synthesized with optimized process parameters shows good response to ammonia in terms of change in resistance (i.e. conductivity). The change in conductivity will change permittivity, which leads to change in the refractive index. The measurement of change in resistance has been carried out at room temperature by indigenously developed computer control gas sensing system. Later on the PPY-PVS film (with optimized parameters) was coated on uncladed region (sensing region) of the PMMA optical fiber. The optical properties of the sensor have been studied by indigenously developed optical fiber gas sensing system and optical fiber test bench. Various parameters viz. sensing probe length, source power and source wavelength have been optimized for enhanced response time and the sensitivity of the sensor.

2. Experimental

2.1. Preparation of optical fiber sensing probe

In the present investigation, we have used a plastic (PMMA) multimode optical fiber (1mm diameter) with core/ cladding dimension 960/40μm. Half meter length of optical fiber was used. The optical fiber sensing probe was prepared by removing the cladding of a small portion (1cm-3cm) of the fiber by polishing with abrasive paper and application of the acetone and water on the fiber and polishing with the tissue [18]. Then it was integrated with a light source (LED) and a Photo detector. The light was focused onto the one end of the fiber and at the other end the light intensity of the fiber was measured. We were continuously monitoring the intensity at the other end of the fiber. We observed sudden fall in intensity at the detector end when the cladding was completely removed (Fig. 2).

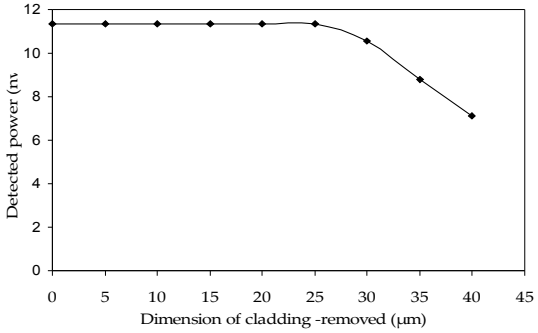

Fig. 2. Graph showing the change in the light intensity as the cladding of the fiber was removed.

2.2. Chemicals used for the synthesis of PPy films

All chemicals used were of analytical reagent (AR) grade. Pyrrole was distilled twice, before use. Pyrrole (99%) and polyvinyl sulphonic Acid (PVS) (25%) was purchased from Aldrich (Germany). Ferric chloride was purchased from Spectro Chem (India) and dopant acids such as p-Toluene Sulphonic Acid (p-TS), Tartaric Acid (TA), hydrochloric Acid (HA), Nitric Acid (NA), Acrylic Acid (AA), Sulphuric Acid (SA) were purchased from Loba Chemie (India). An aqueous solution of pyrrole and ferric chloride was prepared in deionized water.

2.3. Synthesis of Polypyrrole on PMMA substrate

We have synthesized polypyrrole (PPy) film at room temperature on PMMA substrate using chemical polymerization method. The polymerization of pyrrole (monomer) with ferric chloride as an oxidant was performed in aqueous medium (deionized water) containing organic or inorganic dopant such as PVS, p-TS, TA, AA, SA, HA, NA etc for different duration of time. Initially we have optimized the molar concentrations of pyrrole and oxidant. A suitable combination which shows good response to ammonia has been selected for further synthesis.

Then optimized molar concentrations i.e. pyrrole (Py) 0.1M and ferric chloride ($FeCl_3$) 0.05M were used to synthesize the PPy film at room temperature by changing the dopant and its concentration as per Table 1 for different duration of time i.e. 4, 12 and 20 minutes. Pyrrole and $FeCl_3$ were separately dissolved in acidic media

(dopant acid added in deionized water). The PMMA substrate was submerged in the (20 ml) reaction mixture of pyrrole and $FeCl_3$. After few minutes, deposition takes place on the PMMA substrate.

Table 1. Concentrations of monomer (pyrrole), oxidant (ferric chloride) & different dopant acids used for the synthesis of PPy film for 12 minute duration at room temperature.

PPy film	PPy With Dopant	Molar concentration		
		Monomer	Dopant	Oxidant
F1	PPy-PVS	0.1 M	0.012 M	0.05M
F2	PPy-PVS	0.1 M	0.025 M	0.05M
F3	PPy-PVS	0.1 M	0.050 M	0.05M
F4	PPy-pTS	0.1 M	0.025 M	0.05M
F5	PPy-TA	0.1 M	0.025 M	0.05M
F6	PPy-SA	0.1 M	0.025 M	0.05M
F7	PPy-AA	0.1 M	0.025 M	0.05M
F8	PPy-HA	0.1 M	0.025 M	0.05M
F9	PPy-NA	0.1 M	0.025 M	0.05M

2.4. Characterization of Polypyrrole

Synthesized PPy films were characterized using scanning electron microscopy (SEM) at different magnifications by JEOL-JSM-6360A machine, UV-vis and FTIR by Chemito-UV-2100 and Shimadzu-8400 spectrophotometer respectively. This facility was extended by Department of Physics and Chemistry, University of Pune, (MS) India. Synthesized PPy films were subjected to the ammonia gas at room temperature by indigenously developed gas sensing chamber. The electrical conductivity of the PPy film was recorded by conductivity measurement system using four- probe method at room temperature. The current-voltage characterization measurement of the PPy film was recorded by I-V measurement system using four- probe method at room temperature.

3. Results and discussion

The properties of PPy vary with the nature of the dopant anions because the protonation in PPy involves incorporation of anions so as to maintain charge neutrally along the whole polymer backbone. So the optimization of the process parameters viz. concentration of monomer, dopant, oxidant and deposition time etc is important factor. Therefore, in the present investigation we have synthesized the PPy films on the polymethylmethacrylate (PMMA) substrate at room temperature with various concentrations of pyrrole, ferric chloride and various dopant acids for 4, 12 and 20 minutes as per Table 1. Initially all parameters were optimized on the PMMA substrate. Synthesized films were characterized by various techniques as explained previously. Various parameters were optimized for ammonia sensing (in the range 5 to 20 ppm). The PPy films synthesized for 4 minute duration were not uniform and adhesive however the films synthesized for 20 minute duration showed very poor response to lower concentration of ammonia as compared to the films synthesized for 12 minute duration. Therefore the best combinations of optimized parameters were selected for synthesis of PPy-PVS as an active coating on fiber optic sensing probe.

3.1. UV-visible spectroscopy

UV-visible spectroscopy is very sensitive tool for the study of PPy protonation and more precisely for the elucidation of the interaction between doping anions and the polymer chain. The electronic absorption spectra recorded in the range 350-800 nm for all the PPy films F1-F9 synthesized for 12 minute duration at room temperature with various molar concentrations as per Table 1 are depicted in Figs. 3 and 4.

It can be seen from Figs. 3 and 4 that the bands observed between 350 nm and 450 nm and free carrier tail at wavelength greater than 650 nm indicate the formation of PPy in all the films F1 to F9. The absorption at around 630 nm (as bipolaron charge transfer band) indicate conducting nature and absorption at round 450 nm indicate to π-π^* transition. This shows good agreement with the earlier reported work [29, 30].

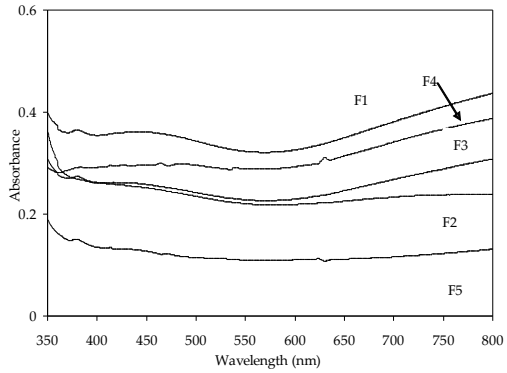

Fig. 3. UV-vis spectrum of PPy films F1-F5 (Table 1) synthesized at room temperature.

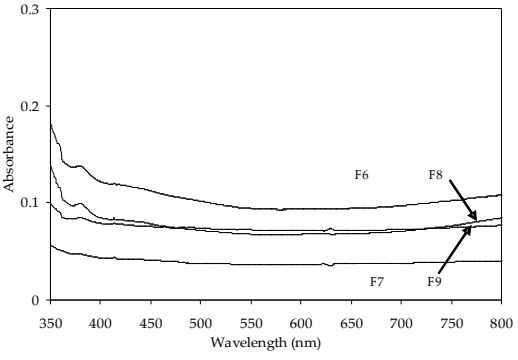

Fig. 4. UV-vis spectrum of PPy films F6-F9 (Table 1) synthesized at room temperature.

3.2. FTIR analysis

Infrared spectrum provides the infrared absorption or transmittance of a film as a function of wave number. The frequencies at which absorption occurs indicate the type of functional groups present in the polymer. Spectrum of all the PPy films synthesized as per Table 1 recorded in the range 500-4000 cm^{-1} shown in Fig. 5.

The spectrum shows broad peaks around 3732 cm^{-1} which correspond to N-H stretching. The peaks at 3180 and 2960 cm^{-1} assigned to $-CH_3$ and $-CH_2$ stretching. PPy ring stretch was observed around 1527 to 1546 cm^{-1}. The bands observed around 1378-1743 cm^{-1} represents C-H out-plane deformation in aromatics and bands around 677-1192 cm^{-1} represents the C-H in plane and C-H out plane deformation in PPy units. All these characteristic bonds confirm the formation of PPy in all the films [31, 32].

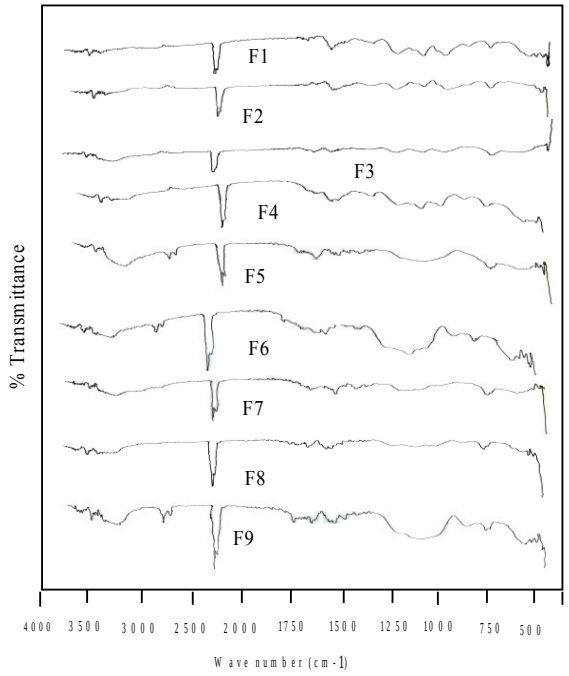

Fig. 5. FT-IR spectrum of PPy films synthesized (Table 1) at room temperature.

3.3. Scanning electron microscopy (SEM) study

We have synthesized PPy films as per Table 1 for various deposition time. We recorded the SEM images of films F1-F9 synthesized as per Table 1 for 12 minute duration at room temperature.

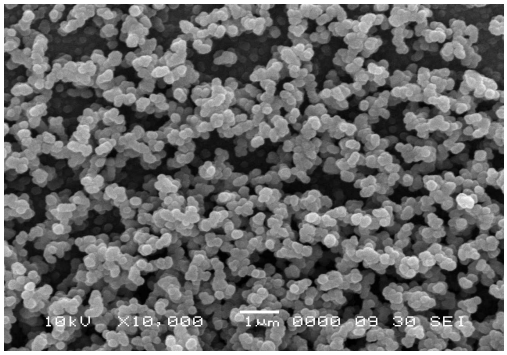

Fig. 6. SEM image of PPy-PVS film (F2) synthesized at room temperature with various molar concentrations as per Table1 for 12 minute duration.

The synthesized PPy films F1, F2, F3 and F8 were uniform and adhesive as compared to other films F4–F6 & F7, F9. However the synthesized PPy-PVS film F2 (Fig. 6) shows more porous, globular and granular surface morphology with good uniformity and adhesiveness (as compared with other films F1 and F3- F9) which is suitable for gas sensing applications [33].

3.4. I-V characteristics

The current–voltage (I-V) characteristics of the synthesized PPy films were studied to ensure an ohmic behavior of the films. A linear relationship of the I-V curve, shown in Fig. 7 reveals that the PPy-PVS film F2 has an ohmic behavior.

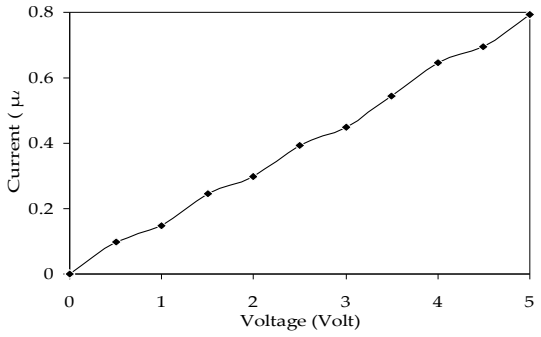

Fig. 7. Current– voltage characteristic curve of synthesized PPy-PVS Film (F2) at room temperature as per Table 1.

3.5. Ammonia sensing characteristics

Sensing behavior of synthesized PPy films F1-F9 (as per Table 1) for ammonia gas was studied at room temperature. It was kept in indigenously developed

computer controlled gas sensing system. The change in resistivity of the film (when exposed to ammonia) was measured at an interval of 10 sec. Interaction of ammonia with PPy increases the resistivity and removal of ammonia decreases the resistivity of the film steadily to a minimum value but a drift from its original value was observed. The sensing behavior in terms of change in resistance (of the PPy films F1-F4 & F6-F9) when exposed to ammonia with different concentrations (5, 10 & 20 ppm) has been studied.

However, film F2 (molar concentrations Py (0.1M), PVS (0.025M), $FeCl_3$ (0.05M)) shows excellent response to 5 to 20 ppm of ammonia with response and recovery time 5 minutes and shows greater change in resistivity when exposed to ammonia gas as compared to other films (Fig. 8). The increase of concentration of ammonia enhances the rate of diffusion of ammonia molecules towards and into the PPy film thereby decreasing the response time. The synthesized PPy-PVS film (deposited on PMMA substrate), with optimized concentrations shows excellent sensing behavior for 5 to 20 ppm of ammonia gas.

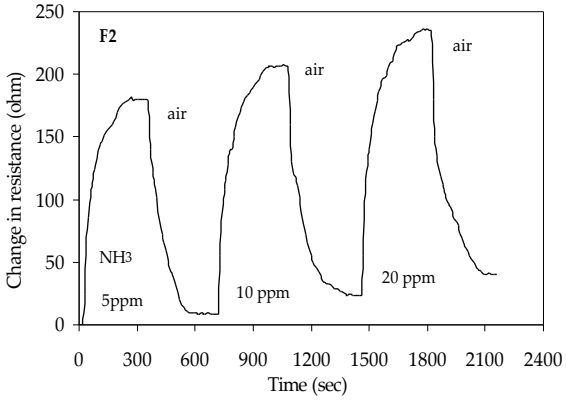

Fig. 8. Sensing behavior of PPy-PVS film (F2) when exposed to ammonia gas for 5, 10 & 20 ppm.

3.6. Deposition of PPy-PVS film on optical fiber sensing probe

The in-situ deposition of the sensitive PPy-PVS film on the modified section of the optical fiber was carried out by suspending the uncladed region (1-3 cm) in the reaction container, consisting of the pyrrole, ferric chloride and dopant acid with the optimized process parameters (Py (0.1M), PVS (0.025M), $FeCl_3$ (0.05M) (Film F2 as per Table 1) for 12 minute at room temperature). Then the resulting coated fiber (Fig. 9) was removed from the solution, washed with deionized water and dried.

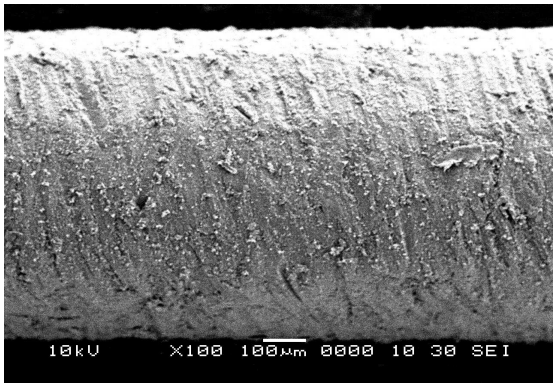

Fig. 9. SEM image of the optical fiber sensing probe coated with PPy-PVS film (F2) synthesized at room temperature as per Table 1.

3.7. Sensing properties of fiber optic ammonia sensor

An experimental set-up used for the characterization of optical fiber sensor was indigenously developed by integrating the optical fiber sensing probe with a light source, a photo detector and other electronic devices. A part of the testing fiber (sensing probe) coated with PPy-PVS film layer was placed in an indigenously developed gas sensing chamber which ensures the contact of the fiber sensing system with vapors. The sensor element was then integrated with a LED light source and a silicon photo-detector (Optical Fiber test bench, Ruby Optosystems, Pune, India). The light source was focused onto the one end of the modified optical fiber sensor. At the other end, a photo detector was positioned to receive the optical signal, and convert the same to an equivalent electrical signal. The change in output power was detected when the sensor was exposed to different concentrations of ammonia vapors (1-10 ppm) at room temperature. The effect of the probe length (1, 2 and 3 cm), source power (1.5, 2.5 and 3.5 µw) and source wavelength (450, 550 and 650 nm) on the sensor response was also investigated.

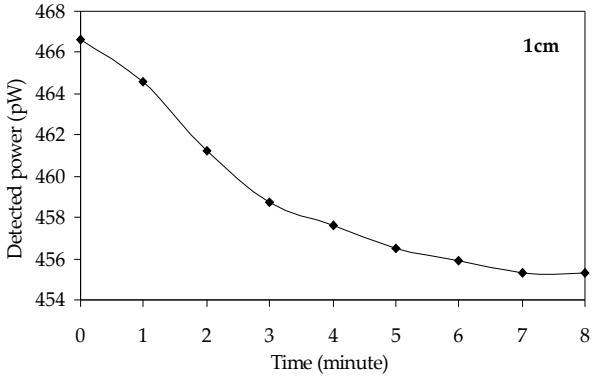

Fig. 10. Sensor response for sensing probe length 1cm.

3.7.1. Effect of length of sensing probe on the sensor response

The sensing probes of length 1 cm, 2cm and 3 cm were prepared and coated with polypyrrole film doped with PVS with the optimized parameters. Figs. 10 to 12 shows the sensor response for sensing probe with different lengths.

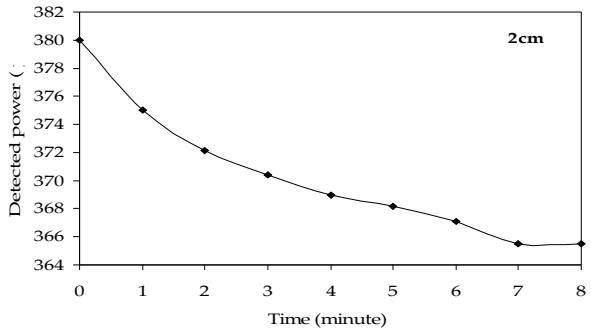

Fig. 11. Sensor response for sensing probe length 2cm.

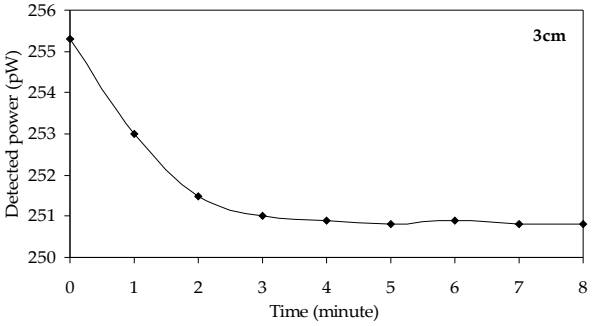

Fig. 12. Sensor response for sensing probe length 3cm.

We observed good response for sensing probe of length 2 cm, source power 3.5μW and source wavelength 650nm, when it was exposed to 5ppm of ammonia vapor. The increase in the sensor response is due to the increase in sensing probe length from 1 cm to 2 cm, however for 3 cm we observed very low sensor response, which may be due to the fact that, more sensing length incorporates more leaky modes and hence less light will interact with the film and thereby decreasing the sensor response.

3.7.2. Effect of wavelength on the sensing response

The response of the sensor in terms of the detected power (with 2cm probe length and 3.5μW source power) for different wavelengths of the source i.e. 450nm, 550nm and 650nm is shown in Fig. 13. We observed excellent response to 5ppm of ammonia for 650nm wavelengths as compared to 550nm and 450nm. This indicates that the sensor response is highly dependent on source wavelength.

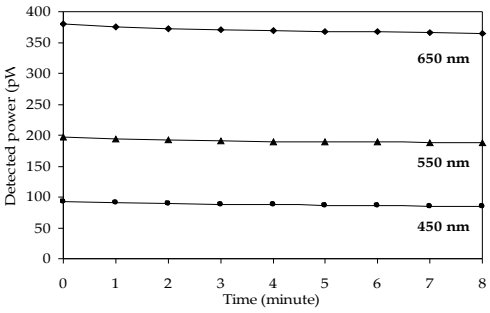

Fig. 13. Response of the sensor with variation in source wavelength.

3.7.3. Effect of source power on the sensor response

The influence of light intensity (of the source) on the sensor response (when it is exposed to 5ppm ammonia vapor) was also investigated. The sensor response observed for source power at 1.5 μW, 2.5 μW and 3.5 μW is shown in Fig. 14. We observed maximum response for 3.5 μW source power. This may be due to fact the more source power has the more evanescent power available at the sensing region which incorporates more interaction with the film.

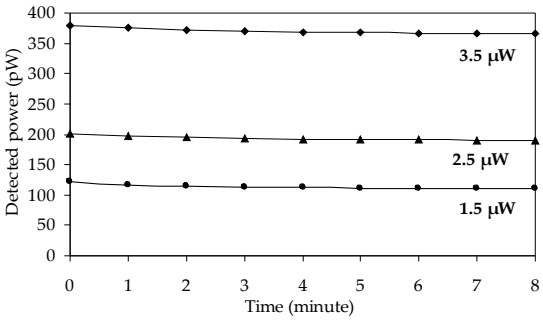

Fig.14 . Response of the sensor for different source power.

3.7.4. Effect of ammonia concentration on the sensor response

We have studied the ammonia sensing behavior of PPy-PVS optical fiber sensor. Fig. 15 shows the response curve of the sensor when exposed to ammonia. For the purpose of investigation of reproducibility and response characteristics of the sensor two measurements were continuously carried out. PPy-PVS optical fiber sensor (2 cm, 650 nm & 3.5 μW) was exposed to 1 ppm of ammonia vapor and detected power was observed. We observed excellent repeatability with 6 minute response and recovery time.

Fig. 16, shows the response of the PPy-PVS optical fiber sensor with optimized parameters for different

concentration of ammonia. It shows linear response for 1 ppm to 10 ppm of ammonia concentration.

Stability and life time of the fiber optic ammonia sensor was also studied and it is shown in Fig. 17. It shows good response to 1ppm of ammonia up to 32 days.

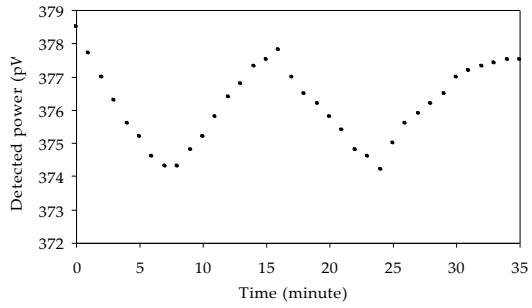

Fig. 15. The response curve of the fiber optic sensor for 1 ppm of ammonia.

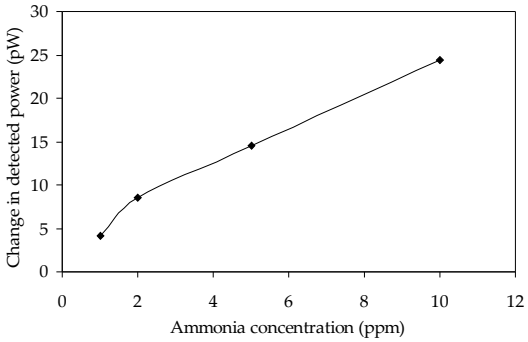

Fig. 16. The response of optical fiber sensor for various ammonia concentrations 1-10 ppm.

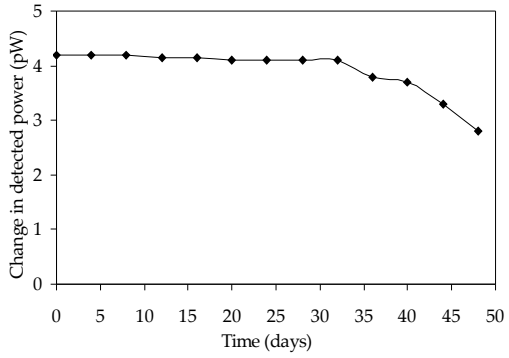

Fig. 17. Stability curve of the PPy-PVS fiber optic ammonia sensor.

4. Conclusions

We have successfully designed and developed (intensity modulated) PPy-PVS fiber optic ammonia sensor which can be used for the detection of lower concentration of ammonia in the exhaled breath of patients with kidney and liver disorder. Ammonia sensitive layer of conducting polymer i.e. PPy-PVS film with optimized process parameters (Py (0.1M), PVS (0.025M), $FeCl_3$ (0.05M) and deposition time 12 minute) deposited on the sensing probe of the plastic (PMMA) multimode optical fiber at room temperature. Sensing response of the sensor to ammonia gas was studied at room temperature. It shows excellent sensing response (with response and recovery time 6 minute) for 1 to 10 ppm of ammonia for probe length 2 cm, source wavelength 650 nm and source power 3.5 μw. It shows almost stable and repeatable response up to 32 days.

Acknowledgement

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