The use of polyaniline nanofiber as modified cladding for fiber optic methanol vapor sensor

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A fiber optic sensor system for detection of methanol vapor was developed. The system is based on the change in the absorption of evanescent wave on core-modified cladding interface during interaction with methanol vapor. In this research, it is used polyaniline nanofiber synthesized by interfacial polymerization as modified cladding. The spectroscopy data show a specific absorbance spectrum of polyaniline nanofiber which changes in the visible range, especially in blue and red bands, when exposed to methanol vapor due to a conformational alignment of polyaniline blackbond structure. The response of the fiber optic sensor was investigated by measuring the transmission light intensity via fiber optic sensor system. It is obtained a very fast response time of 40 s and recovery time of 15 s. The fiber optic sensor also exhibits a good reversibility and repeatability.

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1. Introduction

Most of chemicals vapor including ammonia, alcohols, and hydrocarbon vapors are hazardous and toxic to human health and ecosystems. For example, inhalation of only a small dose of ammonia vapor may cause acute poisoning to people. Threshold limit of ammonia concentration in air is only 25 ppm for human beings [1,2]. On the other hand, alcohols vapors (e.g. methanol vapor) as a kind of volatile organic compound (VOC) may cause poisoning to people [3]. However, alcohols (in many forms) are chemicals that are mostly used in many human activities, in laboratory and industries. Therefore it is important to monitor and control the alcohol vapor leakage [4-6].

Recently, researchers developed various sensor system to detect alcohol vapor, including those based on semiconductivity of materials such as ZnO [7], SnO_2 [8], and Fe_2O_3 [9] or polyaniline nanocomposite material [5]. Another way to detect alcohol vapors by optical method using any materials that change their optical properties (refractive index or absorptivity) when they interact with alcohol vapor, with carbon nanotubes [10], polyelectrolyte [4] dan dyes [11]. In the optical sensor system, there is a rapidly growth of research on fiber optic sensor for chemical vapor or gas detection with different mechanism and configuration [1-3,6]. The development of fiber optic chemical sensors has many advantages, such as real-time, in-situ and remote detection, and the most specific is immunity to electromagnetic interference, and, therefore, low noise [12,13].

In this paper we developed a fiber optic sensor system for detection of methanol vapor based on evanescent wave absorption phenomenon in core/modified cladding interface. To this aim, we used polyaniline nanofiber with modified cladding for plastic fiber optics, because, polyaniline can undergo a conformational alignment when interacts with alcohol vapor that results in the decrease of mass density so that its refractive index decreases [14]. The variation of refractive index of the modified-polyaniline cladding can result in a change of transmission intensity via a fiber optic sensor system. As a different procedure Morisawa et al. have developed a plastic fiber optic sensor to methanol vapor by using swelling polymer material as modified cladding [6].

The principle of the method of evanescent wave absorption is explained as follows. When a light beam propagates along an optical fiber, the electromagnetic field does not abruptly fall to zero at the core/cladding interface. Instead, the overlap of the incoming beam and the internally reflected beam leads to a field that penetrates into the medium next to the core. This electromagnetic field, which tails but does not propagate into the second medium, is called evanescent field. Its intensity $I(z)$ decays exponentially with the distance z perpendicular to the interface as follows [1,12,14]:

$$I_z = I_0 \exp\left(-\, z/d_p\right) \tag{1}$$

where I_0 is the intensity of the incident radiation. The depth of penetration d_p of the evanescent field is related to the angle of incidence θ at the interface, refractive indices of core n_1 and cladding n_2, and the wavelength of the radiation, λ, as follows:

$$d_p = \frac{\lambda}{(2\pi)\sqrt{n_1^2 \sin^2\theta - n_2^2}} \tag{2}$$

The increase of the refractive index of cladding (n_2) leads to the increase of the penetration depth, so that the intensity of evanescent field increases. Based on this phenomenon, we have been inspired to develop a fiber optic methanol vapor sensor by replacing origin cladding of fiber optic with ammonia-sensitive material as modified cladding. In this kind of sensor, the parameter measured is the light intensity carried by the fiber that is modulated by the change in the absorption spectrum of the methanol vapor sensitive cladding that causes a change in penetration depth of evanescent field.

In this research, we used polyaniline nanostructure (nanofiber) as modified cladding to replace the origin cladding of fiber optic. The developed fiber optic methanol vapor sensor is based on change of optical properties (e.g. refractive index) of modified cladding due to conformational alignment of polyaniline structure when exposed to methanol vapor. The use of nanostructural polyaniline, such as nanofibers, could greatly improve the diffusion of methanol vapor molecules, since nanostructural polyaniline has much greater exposed surface area, as well as much greater penetration depth for vapor or gas molecules, compared to their bulk counterparts [13].

2. Experimental details

2.1 Optical fiber preparation

Plastic multi-mode optical fiber with core diameter of 960 μm and cladding diameter of 1000 μm was cut into 100 cm length, and one end of the fiber was equipped with SMA connector and another end was designed as sensing probe element. At about 3 cm from the free end of the fiber (without connector), 2 cm portion was unclad by chemical etching using acetone solution. The unclad portion will be coated with polyaniline nanofiber and acts as sensing element for methanol vapor detection. At the tip end of the fiber was coated with silver paint as reflector.

2.2 Polyaniline nanofiber preparation and coating

Polyaniline nanofiber was prepared by interfacial polymerization method [13,15,16]. The polymerization is performed in an immiscible organic/aqueous biphasic system, containing aniline monomer in toluene solution and aqueous solution of oxidant and dopant solutions. The oxidant used is ammonium peroxodisulphate, $(NH)_4S_2O_8$) and dopant is chloric acid (HCl). As the reaction proceeds, polyaniline forms across the interface, slowly diffusing into the water layer and eventually filling it. At the same time, the color of the organic layer turns red-orange due to the formation of by products, probably aniline oligomers. Allowing the reaction to proceed overnight gives sufficient time to reach completion of polymerization. The product is then collected and purified by filtration, yielding a product in the form of water dispersion or a powder.

For optical characterization and SEM micrographs, polyaniline nanofiber was coated on slide glass by casting method from water suspensions obtained after filtration and washing the polymerizing products. Then, polyaniline nanofiber was coated onto unclad portion of fiber optic core that will be a sensing element for methanol vapor detection.

2.3 Testing set-up of fiber optic sensor

Testing set-up of designed fiber optic sensor shown in Fig. 1, is formed by a bifurcated fiber optic bundle, light source, light detector, interface, and computer (PC) with installed software (DataStudio from PASCO). The designed fiber optic probe by using plastic optical fiber was connected to one end of bifurcated fiber bundle with SMA-SMA connector adapter, whereas the other end with sensing element is immersed into the methanol vapor chamber.

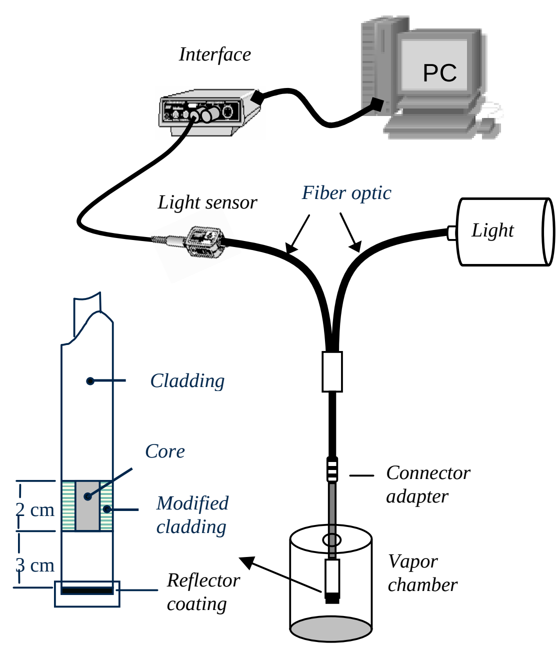

Fig. 1. Set-up for the response measurement of the fiber optic sensor.

The principle of the fiber optic sensor system is explained as follows: Light beam was coupled into one arm of fiber bundle and guided to sensing element, then reflected by silver reflector on the end tip of sensing probe and back to another arm of fiber bundle, so that the beam twice interacts with sensing element. The light beam detected by light sensor is a transmission intensity of light beam after twice interactions with sensing element. Data acquisition and processing were carried out automatically using a software installed in the computer (PC). The obtained data was displayed in cycle curve form that represents a response of sensor system. A cycle curve was obtained by immersing the sensing element into and withdrawing from methanol vapor chamber.

3. Results and discussion

3.1 Surface morphology of polyaniline nanofiber

The surface morphology of the polyanilin nanofiber film cast on glass substrate can be observed directly by using scanning electron microscopy (SEM). The film cast on a glass substrate from polyaniline suspension has fibrous and highly porous morphology as shown in Fig. 2. From SEM image, it is found that these nanofibers are interconnected to form ramose structures, rather than isolated nanofibers. The fibrils diameters and lengths are in the range below 100 nm and below 1 μm, respectively. Their high surface area, porosity, and small diameters may enhance diffusion of molecules and dopants into the polyaniline nanofibers and give significantly better performance in both sensitivity and time response for application in chemical sensor. The nanofibrous and highly porous structure, allows vapor molecules to penetrate through the entire layer and interact with all the polyaniline nanofibers. Therefore, all the fibers are able to contribute to the sensing process to obtain good sensitivity.

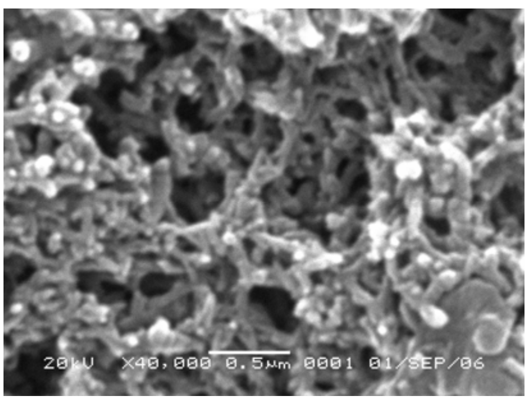

Fig. 2. Morphology of polyaniline nanofiber by SEM.

3.2. Optical characteristic of polyaniline film

Fig. 3 shows the specific absorption spectra of polyaniline nanofiber film on glass substrate without and with exposure to methanol vapor, respectively. This spectroscopyical result shows a specific absorbance spectrum of polyaniline film (without exposure to vapor). The film strongly absorbs the narrow blue band and broad red band spectra. There are two absorption peaks for the polyaniline at about 430 nm and 850 nm, and this agrees with doped polyaniline (emeraldine salt).

The polyaniline nanofiber film shows significant optical absorbance changes upon exposure to methanol vapor at room temperature, as shown on absorbance spectra at Fig. 3. At a visible wavelength range, the absorbance changes with methanol vapor presence, especially in the ranges of the blue band and red band spectra. It is observed a decrease of absorbance at narrow blue band spectra, whereas at the broad red band spectra the absorbance increases. On the other hand, the absorbance in the green spectra does not change. This means that the polyaniline film does not change in color. So, the changes of absorbance spectra are due to changes in the refractive index of polyaniline due to the interaction with methanol vapor. It is believed that interaction between polyaniine with methanol vapor molecules leads to conformational alignment in the backbone of polyaniline structure that results in the modification of the refractive index [14].

As a result, the visible optical sensing method using conducting polyaniline nanofiber demonstrates the possibility of application of methanol vapor sensor. By employing absorbance measurement as a vapor detection method, it will be possible to develop an optical methanol vapor sensor. For a fiber optic sensor system, polyaniline nanofiber will be successfully applied as modified sensitive cladding for methanol vapor sensors.

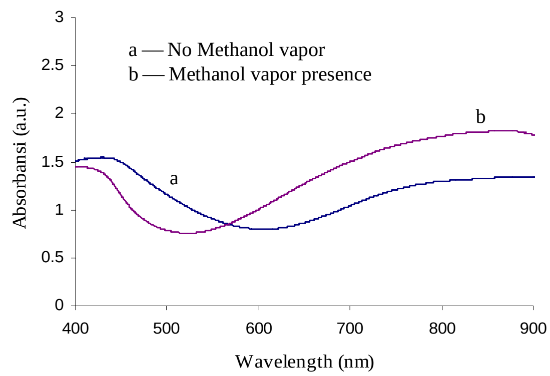

Fig. 3. Absorbance spectra of polyaniline nanofiber film (before and after exposure with methanol vapor).

3.3. Response characteristics of designed sensor

To investigate the response time, recovery time, and reversibility, the response of optical fiber sensor to methanol vapor was characterized in the presence of methanol vapor. The response curve in Fig. 4 shows three cycles curve, which describes the change of transmission intensity of light beam via fiber optic sensor. It shows that the transmission light intensity rapidly increases when the sensor probe is immersed into the methanol vapor chamber due to the decrease of the refractive index of polyaniline cladding by interaction with methanol vapor. The decreasing refractive index of modified-polyaniline cladding due to the conformational alignment of polyaniline structure [14], that results in the decrease in the penetration depth of evanescent field at the modified cladding as absorption part of intensity, so the transmission light intensity via fiber optic increases.

When the sensor probe (with modified cladding) is withdrawn from the methanol vapor chamber, the transmission light intensity drops abruptly to initial stationary value. The phenomenon called "recovery", where the polyaniline cladding goes back to initial condition with initial refractive index when the methanol vapor is lacking.

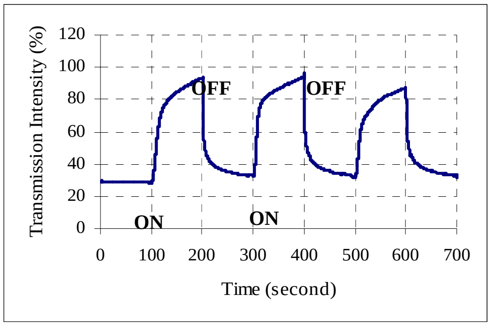

Fig. 4. Response of fiber optic ammonia sensor.

The response time depends on the time required for methanol vapor to diffuse through the fibrous and highly porous structure of polyaniline. When the methanol vapor is introduced, the methanol molecules diffuse effectively into the nano-fibrous structure of the polyaniline as modified cladding of fiber optic. One believes that the use of polyaniline nanofiber as a modified cladding, the methanol vapor molecules can penetrates effectively into modified cladding so the nanofibers of polyaniline can contribute in the sensing mechanism. Therefore, the sensor has an optimized response time and recovery time.

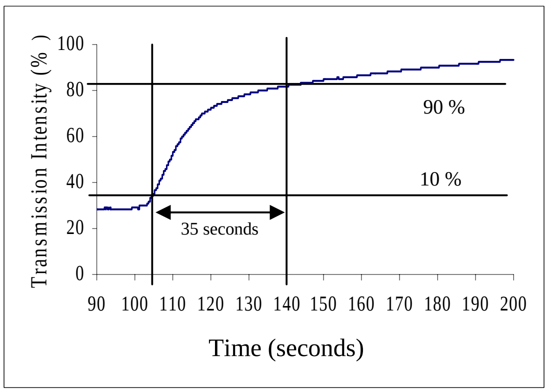

Fig. 5. Response time curve of sensor probe for methanol vapours.

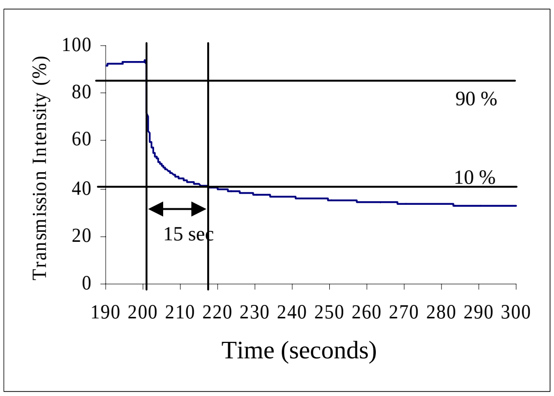

Fig. 6. Recovery time curve of sensor probe.

Based on the definition of response time that is determined by the time interval between 10% and 90% of the stationary value of response curve [1], the response time of the optical sensor to analyte (methanol vapor molecules) is found 35 s (Fig. 5). In the same way, the recovery time is identified to be about 15 s (Fig. 6). Regarding these values, we observe that the designed fiber optic sensor has a very fast response to methanol vapor. Therefore, we conclude that the designed sensor can rapidly detect the presence and absence of methanol vapor. We also found that the response time is slightly less than recovery time because the polyaniline cladding needs more time to align the conformation of polyaniline backbone structure than recover to initial condition.

Regarding the response curve, the designed fiber optic methanol vapor sensor exhibits a good reversibility and repeatability as shown in during cycling. This means that designed fiber optic sensor has a reversible and repeatable characteristic that are the main sensor requirements.

4. Conclusion

We have designed and developed an intrinsic fiber optic methanol vapor sensor based on evanescent wave absorption using polyaniline nanofiber as modified cladding. The sensing properties of polyaniline nanofiber film coated on glass substrate were investigated by spectrophotometry. The film exhibits a change of the absorbance spectrum during methanol vapor exposure. The fiber optic sensor were designed by replacing the origin cladding of a plastic fiber optic with polyaniline nanofiber coating at about 2 cm from one end of the fiber optic. A very fast response time about 35 s and recovery time of 15 s were obtained. This result have demonstrated a fast response fiber optic ammonia vapor sensor due to the use of nanostructured polyaniline as modified cladding for optical fiber. The polyaniline nanostructure cladding facilitates an effective diffusion of ammonia gas molecules to enhance the sensitivity of designed fiber optic sensor.

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