

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

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It has been developed a fiber optic sensor system for detection of methanol vapor. The system was based on the change in the absorption of evanescent wave on core-modified cladding interface when interacts with methanol vapor. In this research, used polyaniline nanofiber synthesized by interfacial polymerization as modified cladding. The spectroscopy result show a specific absorbance spectrum of polyaniline nanofiber was change in the visible range, especially in blue and red bands, when exposed with methanol vapor due to a conformational alignment of polyaniline blackbond structure. Response of the designed 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]. 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 the chemicals that mostly used in many human activities, as in laboratory and industries, therefore it needs to monitor and control the alcohol vapor leakage [4-6].

Recently, many researchers developed sensors systems to detect alcohol vapor, including those based on semiconductivity of materials such as ZnO [7], SnO₂ [8], and Fe₂O₃ [9] or polyaniline nanocomposite material [5]. Another way to detect alcohol vapors by optical method using materials that change their optical properties (refractive index or absorptivity) during interaction with alcohol vapor, including carbon nanotubes [10], polyelectrolyte [4] dan dyes [11]. In the optical sensor system, it is a rapid growth of researches on fiber optic sensor for chemical vapor or gas detection with different mechanisms and configurations [1-3,6]. Development of fiber optic chemical sensors have many advantages, such as real-time, in-situ and remote detection, and the most specific is the immunity to electromagnetic interference, therefore they have 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. For this aim, we used polyaniline nanofiber as modified cladding for plastic fiber optic, because, polyaniline can undergo a conformational alignment when interacts with alcohol vapor that results in the decrease of mass density, and the decrease of the refractive index value [14]. Variation of refractive index of the modified-polyaniline cladding can result in a change of transmission intensity via a fiber optic sensor system. Morisawa et al. [6] have developed a plastic fiber optic sensor to methanol vapor by using swelling polymer material as modified cladding.

The principle of evanescent wave absorption method 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]:

$$I_z = I_0 \exp\left(-\frac{z}{d_p}\right) \quad (1)$$

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:

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

Increase in the refractive index of cladding (n_2) leads to the increase the penetration depth, so that intensity of evanescent field increase. Based on the phenomenon, we developed 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 the 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 based on the modification 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 nanostructure polyaniline, such as nanofibers, could greatly improve diffusion of methanol vapor molecules, since nanostructure polyaniline has much greater exposed surface area, as well as much greater penetration depth for vapor or gas molecules, relative 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, which one end of the fiber was equipped with SMA connector and another end will be designed as sensing probe element. 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 adopted from some references [13,15,16]. The polymerization is performed in an immiscible organic/aqueous biphasic system, comprises of aniline monomer in toluene solution and aqueous solution of oxidant and dopant solutions. The oxidant used is ammonium peroxodisulphate, ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) 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 byproducts, probably aniline oligomers. Allowing the reaction to proceed overnight gives it 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, respectively.

For optical characterization and SEM photography, 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 at Fig. 1, comprises of 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 immerse into the methanol vapor chamber.

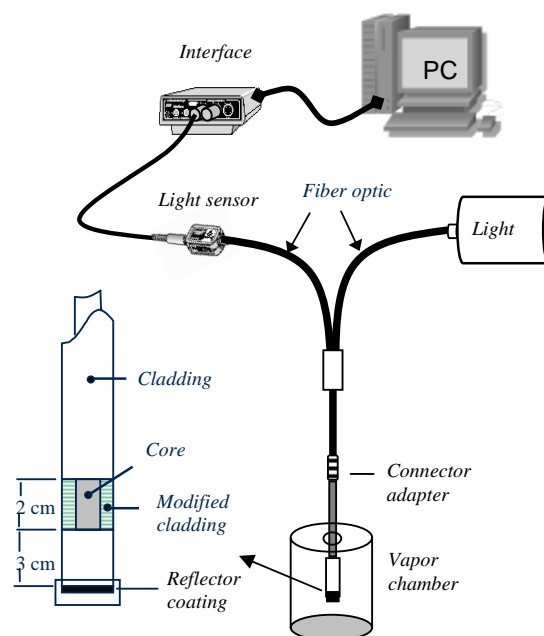


Fig. 1. Set-up for response measurement of fiber optic sensor.

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 interacts with sensing element. Data acquisition and processing were carried out automatically using software installed in the computer (PC), data obtained was displayed in cycle curve form representing a response of sensor system. A cycle curve was obtained by immersion of the sensing element into and withdraw from methanol vapour chamber.

3. Results and discussion

3.1 Surface morphology of polyaniline nanofiber

The surface morphology of the polyaniline 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 at Fig. 2. Regarding 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, which 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.

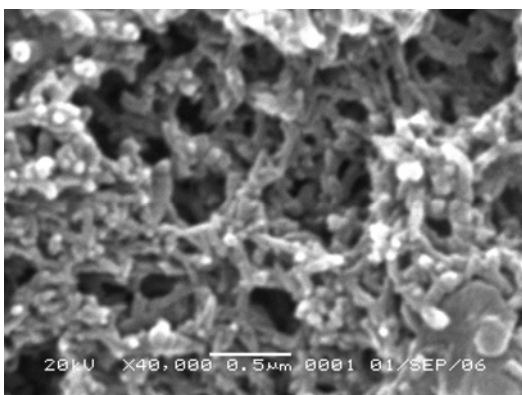


Fig. 2. Morphology of polyaniline nanofiber by SEM.

3.2. Optical characteristic of polyaniline film

Fig. 3 shows the specific absorption spectra of polyaniline nanofiber film on glass substrate, respectively without and with methanol vapor exposure. This spectroscopy result shows a specific absorbance spectrum of polyaniline film (without vapor exposure), it is 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 a significantly 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. That is why shows a decreases 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 changes in color. So, the changes of absorbance spectra due to change in the refractive index of polyaniline determined by the interaction with methanol vapor. It is believed that interaction between polyaniline with methanol vapor molecules leads to conformational alignment in the backbone of polyaniline structure that results in the refractive index change [14].

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

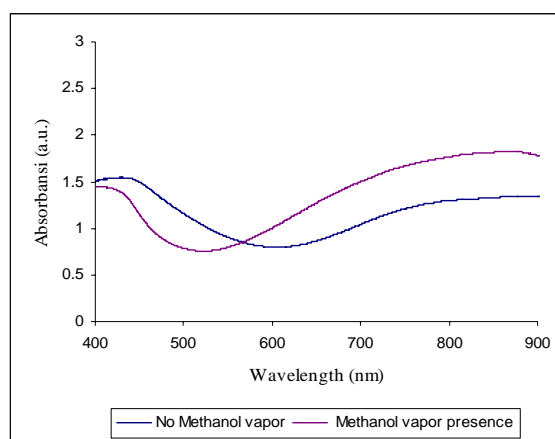


Fig. 3. Absorbance spectra of polyaniline nanofiber film (before and after exposure with methanol vapor).

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 methanol vapor presence. The response curve at Fig. 4 shows three cycles curve, which represents change of transmission intensity of light beam via fiber optic sensor. It show that the transmission light intensity rapidly increase when the sensor probe immerse into the methanol vapor chamber due to the decreasing 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 result in the decrease in the penetration depth of evanescent field at the modified cladding as absorption portion of intensity, so the transmission light intensity via fiber optic increase.

Then, when the sensor probe (with modified cladding) is withdrawn from the methanol vapor chamber, the transmission light intensity abruptly drop to initial stationary value. The phenomenon is called recovery, where the polyaniline cladding back to initial condition with initial refractive index when without methanol vapor.

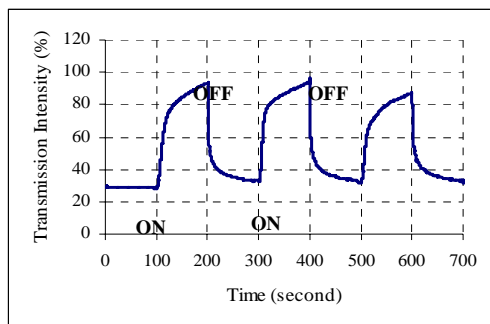


Fig. 4. Response of fiber optic ammonia sensor.

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 was introduced, the methanol molecules diffuse effectively into the nano-fibrous structure of the polyaniline as modified cladding of fiber optic. It is believed that the use of polyaniline nanofiber as a modified cladding, the methanol vapor molecules can penetrate effectively into modified cladding so the nanofibers of polyaniline can contribute to the sensing mechanism. Therefore the sensor has an optimized response time and recovery time.

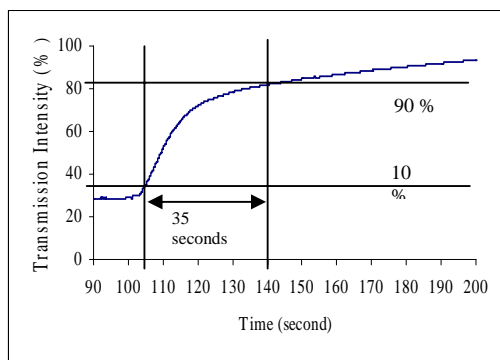


Fig. 5. Response time curve of sensor probe.

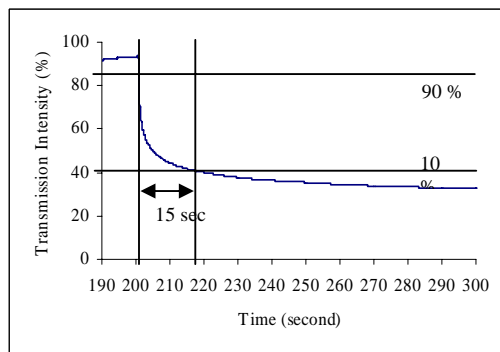


Fig. 6. Recovery time curve of sensor probe.

Based on the definition of response time that is determined by the time interval between the 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 of 35 s (Fig. 5). In the same way, the recovery time is identified to be about 15 s (Fig. 6). Regarding these values, we know 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 of the polyaniline cladding needs more time to align the conformation of polyaniline backbone structure than needs the recovery to initial state.

Regarding the response curve, the designed fiber optic methanol vapor sensor exhibits a good reversibility and repeatability as shown in cycle curve. It means that the designed fiber optic sensor has a reversible and repeatable characteristic as one of sensor requirements.

4. Conclusions

We have designed and developed an intrinsic fiber optic methanol vapor sensor based on evanescent wave absorption using polyaniline nanofiber as modified cladding. Sensing properties of polyaniline nanofiber film coated on glass substrate were investigated by spectrophotometer, the film exhibits an absorbance change of spectrum by methanol vapor exposure. The fiber optic sensor was 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 demonstrated a fast response fiber optic ammonia vapor sensor due to use of nanostructured polyaniline as modified cladding for fiber optic. The polyaniline nanostructure cladding facilitates an effective diffusion of ammonia gas molecules to enhance sensitivity of designed fiber optic sensor.

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