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Ammonia level sensor using tapered optical fiber coated with titanium dioxide-incorporated porphyrin

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Since ammonia is water-soluble, environmental studies have shown that the industrial waste such as fertilizer manufacturing, food products, palm oil, urea fertilizer industry can cause very serious damage to water body ecosystems if not properly managed, resulting in a decrease in water quality. Devices based on optical technology, especially devices that combine optical fibers and nanomaterials, are identified as highly sensitive to the species of interest by detecting changes in physicochemical properties. A practical, easy-to-use, inexpensive instrument for detecting ammonia level was proposed using tapered optical fiber (TOF) coated with titanium dioxide-incorporated porphyrin. TOF was fabricated by simultaneously stretching and heating. The preparation of TiO_2/porphyrin/gelatine was prepared to coat tapered optical fiber by dipping. SEM analysis shows an increase in length and a decrease in diameter, also the successful coating of titanium dioxide and porphyrin in the taper region. The EDX analysis also proves the presence of the Ti element in the TOF layer. The TOF produces significant sensing performances toward the ammonia liquid concentration level. The TOF coated with titanium dioxide-incorporated porphyrin can detect a one ppm difference in ammonia concentration with a certain range of output voltage for every concentration has.

Keywords: ammonia sensing, tapered optical fiber, titanium dioxide, porphyrin.

1. Introduction

Ammonia is a chemical compound with a highly hazardous disposition that requires proper monitoring methods. Environmental studies have shown that ammonia waste can cause significant environmental damage, contribute to acidification or eutrophication processes, and affect human health [1,2]. In the case of poor management, the industrial waste may lower water quality, even bring grave damage to water body ecosystems [3,4]. Considering there are various sources such as fertilizer manufacturing, food products, palm oil, urea fertilizer industry, especially since ammonia is water-soluble, developing the detection system is the focus of the current researchers. Optical fiber-based sensors have advantages such as high measurement accuracy, indirect contact, practically non-electric [5], smaller size, biocompatibility, multiplexing, remote sensing capability [6], and the possibility of real-time monitorization [5,6], which is vital in industrial processes [7].

One easy method to fabricate fiber optic sensor is by reducing certain area of the fiber. For single mode optical fiber, cladding is commonly used to lessen the penetration of the electric mode into surrounding medium in propagating mode. Thus, tapering allows the core and the diameter to be the same in proportion which leads to light coupling from the main mode of the normal fiber to modes of the tapered that interacts with the surrounding medium [8]. The modified optical fiber in the form of tapered optical fiber (TOF) supports greater power loss to enhance the evanescent waves that come out of the propagation mode to scatter and interact with the surrounding medium so as to increase sensitivit y [9]. Coating the sensitive material on the TOF will change the optical characteristics of the sensitive layer, such as the optical spectrum obtained from the fiber, thus permits the use of tapered fiber for various sensing applications [10]. An interesting example is the use of organic dyes, such as porphyrin, as active elements, which can work at room temperature [8, 9] and can be optically monitored [10,11]. Titanium dioxide and porphyrin can be used as sensitive layer [12] in which porphyrin has high selective properties to interact with certain compounds, such as ammonia [13]. In this work, we propose a sensor for the detection of liquid ammonia level using TOF coated with titanium dioxide-incorporated porphyrin.

2. Materials and method

The fabrication process of tapered optical fiber in this study was obtained by stretching and heating method using autograph. This study not only focus on the work function of the TOF sensor, but it is also detailed on the fabrication of the TOF to get a reproducible sensor by measuring many parameters during the fabrication. First, the cladding part of the optical fiber (FD 620-10 from Autonics, USA) was peeled off, leaving only the core. The optical fiber was clamped on both ends the end, and the peeled part was heated at 70°C. During the heating process, the optical fiber was pulled slowly to obtain desired diameter due to the elongation. The preparation of TiO_2/porphyrin used 0.140 gram of TiO_2 powder (Merck, Germany) which was dissolved in water in the beaker glass to dissolve TiO_2. In another glass beaker, 0.056 gram of porphyrin (Hach, USA) was dissolved in water with a ratio of 1:1.

Preparations of various concentrations of TiO_2/porphyrin of 70/30, 60/40, 50/50, 40/60, and 30/70 were done by mixing for 10 minutes. Here, 0.8 ml of gelatin with concentration of 20% was given to the mixture so TiO_2/porphyrin can stick to the fiber by having homogeneous solution. Tapered optical fiber was then coated with TiO_2/porphyrin by momentarily dipped in the solution, and dried for one hour at room temperature. The process was repeated ten times with the last drying left overnight. Here, TiO_2 would be the matrix while the porphyrin seeped into the gap.

Characterization using SEM-EDX was carried out to determine the surface morphology, and to check whether the coating material, *i.e.*, TiO_2 and porphyrin fibers completely coated the optical fiber by analyzing quantitatively the percentage of each element. The tapered optical fiber was evaluated by setting it up using Arduino Uno to measure the output voltage. A light source (SYD1230 from Sacher Laser) with wavelength range around 650 nm was set up and connected to a tapered fiber. The intensity of transmitted light through tapered fiber was measured by light dependent resistors (LDR) sensor and then calculated by Arduino Uno to read the output voltage, the value then was displayed on the LCD.

3. Results and discussion

In this study, we prepared the tapered optical fiber by heating and stretching method. The core-only optical fiber was pulled and heated at the same time with speed of 2 mm/min and temperature of 70°C. The optical fiber was pulled until it reached the plastic deformation area to obtain the mechanical properties. Investigating mechanical properties, like tensile strength and modulus elasticity, of our material as ammonia level sensor is extremely important to acquire the information of how our materials behave, especially when subjected to a force. As seen in Fig. 1, we could evalute the changes from stress-strain graph to obtain the information that the optical fiber has tensile strength of 46.26 MPa and modulus elasticity of 4.22 GPa. Due to its measurable parameters during the fabrication, it can be confirmed that the TOFs fabrication is reproducible.

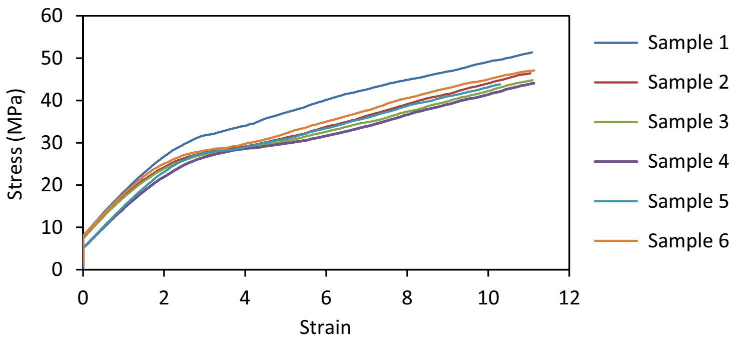

Fig. 1. Stress-strain graph of tapered optical fiber.

Tapered optical fiber was then coated with TiO_2/porphyrin by momentarily dipped in the solution, and dried for one hour at room temperature. The process was repeated ten times with the last drying left overnight. EDX was used to quantitatively analyze the percentage of each element as seen in Fig. 2. It showed that there are elements C, O, Ti, Na, and Mo. The C and O atoms were found to be in majority, with the C atomic composition of 45.08% and the O atomic composition of 44.74%. Then, there was Ti with atomic composition of 7.11%. The composition of C and O atoms dominates because of the polymer structures, which were from optical fibers, gelatin, and porphyrin

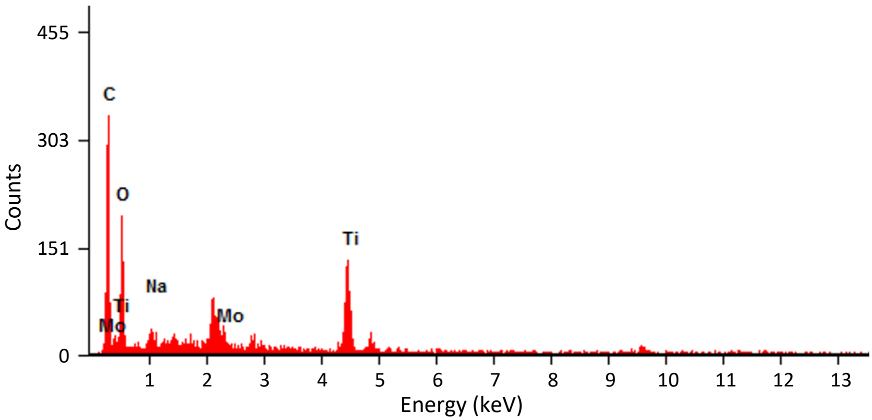

Fig. 2. EDX results of TOF with titanium dioxide-incorporated porphyrin layer.

that are composed of many C, O, and H atoms, also the O atom contribution from TiO_2. There were other elements found, namely Na with atomic composition of 2.38% and Mo with atomic composition of 0.7%. The small presence of Na and Mo elements was assumed due to the impurities.

We investigated the obtained tapered optical fiber (TiO_2/porphyrin, 70/30) by SEM as shown in Fig. 3. The observation was magnified by 50 times and showed the shrinking of the optical fiber. We obtained an increase of 23.83% in length and a decrease of 18.60% in diameter that is due to the process of heating and stretching. By having smaller diameter, we suggested that the performance of the optical tapered optical fiber would be better because the sensor probe area would be sensitive to the surrounding environment as it was mentioned in previous research [14]. The light from the fiber-core coupled with nanostructure region improves the optical interaction be-

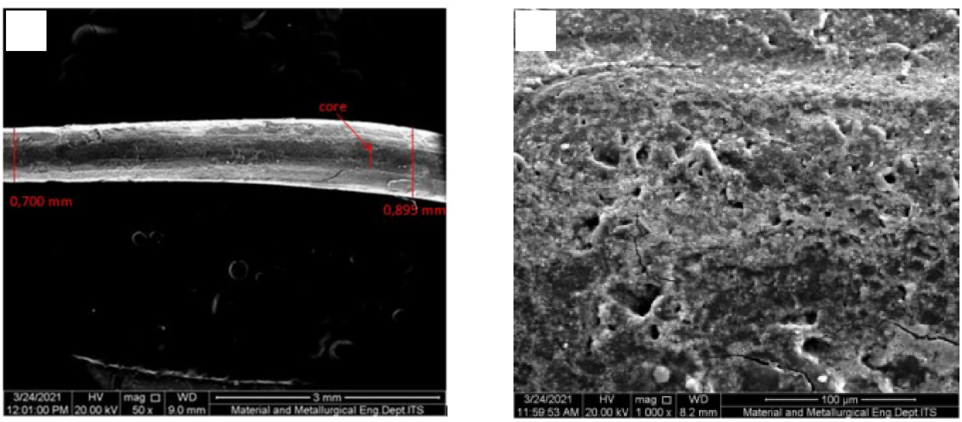

Fig. 3. SEM image TOF with titanium dioxide-incorporated porphyrin layer with (a) 50×, and (b) 1000× magnification.

tween the device and the surrounding environment. Specifically for TiO_2 nanoparticles, when deposited onto particular area of a substrate, cause unique enhancement in the interface between the substrate and TiO_2, which advances sensitivity to external changes [15]. Porphyrin molecules with rapid electron injection and exceptional chemical stability, have the ability to spontaneously connect to TiO_2 nanoparticles by bridging ester-like or bidentate interactions, which is extremely advantageous in photoelectrochemistry [16].

As mentioned previously, in order to be used as an ammonia level sensor, one of the most important component is the sensitive layer that changes its properties in response to the presence of a particular analyte [1]. Characteristics such as sensitivity or response time are highly dependent on the performance and characteristics of the sensitivity layer. Porphyrins are ideal candidates due to their characteristic like absorption, emission, charge transfer, and complexing properties due to the special ring structure of conjugated double bonds [17]. In our research we increased the sensitivity of our sensor by coating the optical fiber with TiO_2/porphyrin. Due the coating process, we increased the magnification by 1000 times to observe the surface of tapered optical fiber as shown in Fig. 3. It was proved that the layer of tapered optical fiber was layered by TiO_2/porphyrin with TiO_2 as the matrix while the porphyrin seeped into the gap and would interact with analyte later. It was also shown that there were pores on the layer which would make the coated tapered optical fiber interact with ammonia better and faster. Interaction between the porphyrin and the titanium dioxide becomes stronger in the ammonia atmosphere and the formation of the complex ion leads to a change in the refractive index of the coating [1].

The majority of sampling techniques are taken off-site to a lab for examination. These sampling techniques may be exceedingly expensive, time-consuming, and risky for the sample's integrity during collection, transit, storage, and analysis. To achieve monitoring so that the samples may be analyzed in the field, portable, reliable, and accurate techniques of analysis are required. Light dependent resistors (LDR) are passive devices that usually use photoconductive materials with ability to change the conductivity of the material in response to variations in irradiance. The properties of these sensors indicate that direct measurements of irradiance or illuminance are possible on experiments. Their basic operation does not require any knowledge of electronics. When light is shed on the device, the rate of excitation increases, and with it the electrical conductivity. Therefore, this relationship between incident irradiance and conductivity or resistivity can be determined in such a way that these sensors can be used as a measurement tool for optics experiments [18]. Porphyrins can be used for chemical sensing, in which it interacts with the modifying chemical analyte and changes the physical properties of a porphyrin into a measurable signal. Based on the signal transductions, porphyrin chemosensors utilizing optical, electrical, even acoustic properties have been developed [19]. In particular, electrical conversion-based porphyrin sensors such as chemical resistors like ChemFet are of interest by taking advantage of the properties of porphyrin semiconductors. This characteristics of resistance can be measured by setting up light detector using a light source and light dependent resistor, in which it is measured by a microcontroller. The greater is the light intensity hiting the resistor the lower is the resistance value, making the current flow easier. This mechanism can be provided by converting the intensity into voltage [20,21], specifically output voltage that is detected by the microcontroller. It is a very common method to convert the output intensity into output voltage due to ease instruments.

During the process of making TiO_2 coating with porphyrins, porphyrins are bound in the TiO_2 matrix through an ion exchange reaction (substitution) of 4 anions from porphyrins with 4 proton bonds from the TiO_2 matrix. When the TiO_2/porphyrin mixture is exposed to ammonia solution, the bond between the two components can increase because the TiO_2 layer is negatively charged due to the presence of hydroxide ions [13].

$$\text{Ti-O-Ti} + H_2O \rightarrow 2\text{TiOH} \tag{1}$$

$$\text{TiOH} + H^+ \rightarrow \text{TiOH}_2^+ \tag{2}$$

$$\begin{aligned} &4\text{TiOH}_2^+ + \text{TMPyP}^+ (4\text{p-CH}_3\text{-ph-SO}_3^-) \rightarrow \\ &\quad \rightarrow 4\text{TiOH} + \text{TMPyP}^+ + 4\text{p-CH}_3\text{-ph-SO}_3\text{H} \end{aligned} \tag{3}$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \tag{4}$$

$$\text{TiOH} + OH^- \rightarrow \text{TiO}^- + H_2O \tag{5}$$

Based on the above equilibrium reaction equation, the electrostatic bond between the porphyrin and the TiO_2 matrix becomes stronger in the composite layer and the formation of complex ions leads to a change in the refractive index, which affects the detected power transmission. Porphyrins have high selectivity for the presence of the target analyte and low sensitivity to non-amine substances [13]. We measured the out-

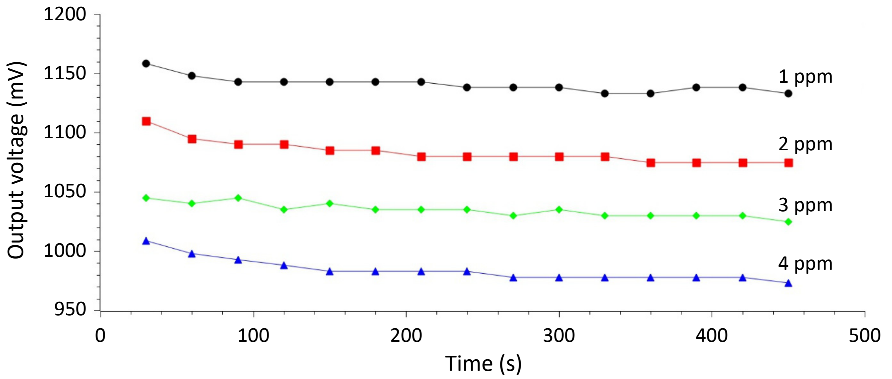

Fig. 4. Output voltage of TOF with titanium dioxide-incorporated porphyrin layer over time for ammonia concentration of 1 to 4 ppm.

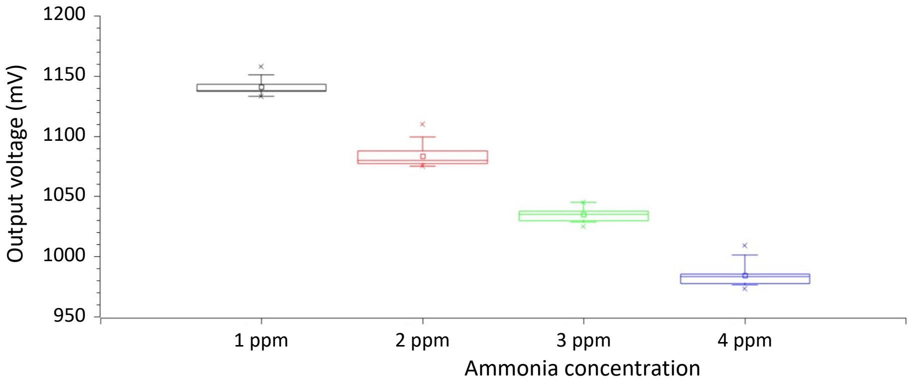

Fig. 5. Output voltage of TOF with titanium dioxide-incorporated porphyrin layer for ammonia concentration of 1 to 4 ppm shown as boxplots.

put voltage of tapered optical fiber (TiO_2/porphyrin, 70/30) while detecting different ammonia concentrations (1–4 ppm). Data were collected by recording the output voltage every 30 seconds for 7.5 minutes (see Fig. 4). The results suggested the change in output voltage due to change in refractive index of the coating upon exposure to ammonia in the solution as mentioned previously. The output voltage detected was seen to be quite stable over time. Thus, we proposed different levels of ammonia concentration as shown by the boxplots. Based on the results showed as boxplot (see Fig. 5), we can identify even down to 1 ppm difference of ammonia concentration since every concentration has certain range of output voltage such as 1158–1133 mV for 1 ppm, 1110–1075 mV for 2 ppm, 1045–1025 mV for 3 ppm, and 1009–973 mV for 4 ppm.

4. Conclusions

We proposed a practical ammonia level sensor using tapered optical fiber coated with titanium dioxide-incorporated porphyrin. The fabrication can be easily done by stretching and heating to produce TOF of the desired diameter. Due to measurable parameters, it is easier to conclude that the TOF fabrication is reproducible. The SEM analysis shows an increase in length and a decrease in diameter, also the successful coating of titanium dioxide and porphyrin in the taper region. The EDX analysis also proves the presence of the Ti element in the TOF layer. The TOF produces significant sensing performances toward the ammonia liquid concentration level. The TOF coated with titanium dioxide-incorporated porphyrin can detect one ppm difference in ammonia concentration since every concentration has a certain range of output voltage.

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