# ZnO and GO coated plastic optical fiber for low concentration of ethanol detection in beer

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Ethanol is widely used in food industry, pharmaceutical industry, cosmetic and fragrance industry. This paper reports on the fabrication of ethanol sensor based on ZnO and GO coated plastic optical fiber (POF). ZnO and GO were synthesized by using simple and low-temperature Hydrothermal Method and Modified Hummers' method, respectively. ZnO shows a hexagonal wurtzite structure based on XRD spectra, meanwhile nanorods shape is observed by using FESEM. This sensor operates based on evanescent wave absorbance principle. The cladding of the fiber is removed by using diluted acetone and sandpaper. The performance of ZnO and GO coated POF towards 0.5% to 3.5% of ethanol were analyzed and compared with uncoated POF. GO coated POF exhibit the highest sensitivity which is 0.2349 a.u/% compared to POF coated with ZnO with a value of 0.0697 a.u/%. The limit of detection of GO coated POF is 1.29% with slope linearity of 89%. Thus, GO coated POF had been selected for the detection of real Beer sample.

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## 1. Introduction

Alcohol in chemistry perspective is an organic compound consists of carbon, hydrogen and oxygen. The general formula of alcohol is R-OH where the functional group of hydroxyls (OH) is bind with carbon atom. Alcohol generally referred to as ethanol in food labeling as it is the compound that responsible to give intoxicant to the consumer. Not only that, ethanol is the common components found in the fermentation process [1]. Nowadays, with the development of technology, ethanol is widely used in industry such as food industry, pharmaceutical industry and cosmetic and fragrance industry. Beers is the products of alcoholic fermentation, a process of anaerobic conversion of sugars mainly glucose and fructose to ethanol and carbon dioxide. Under regulation 361 of the Food Act 1983 and the Food Regulation 1985 in Malaysia, alcohol is a liquid containing more than 2% (v/v) alcohol content [2].

POF exhibit higher elasticity, flexibility and low cost over glass optical fiber (GOF) [3] where these properties make the POF one step ahead in sensor application. Fiber optic sensor can be divided into two classifications which are extrinsic and intrinsic sensors. The optical signal from extrinsic part leaves the waveguide first to enter the sensing probe then re-enter the next waveguide and perform a modulation process. Due to this process, the light is gathered and transmitted for use of detection. Differ from extrinsic sensor, the optical signal of intrinsic sensor does not leave the waveguide. Instead, it is reflected at the entrance side known as reflection system or transmitted to the other side called as transmission system. A reflection system uses absorption, fluorescence, light scattering, refractive index and intensity fluctuations among other things to detect target parameters for intrinsic sensors [4]. Meanwhile transmission systems can make control of evanescent wave absorption to monitor changes on the fiber's surface. Evanescent wave absorbance is a popular analytical method in fiber sensor based on attenuation of total internal reflection. Sensors that operated through this method operated by penetration of evanescent wave into the cladding region and the surrounding medium. This is achieved by removing a part of cladding fiber allowing direct interaction between light at the core with the surrounding medium [5].

Zinc Oxide (ZnO) is a semiconductor metal oxide with hexagonal wurtzite-type structure. ZnO exhibit in the form of variety nanostructure from nanoporous, nanotubes, nanowire [6], heterojunction, thin layer, thick layer, sintered pallets or single crystal [7]. ZnO has a large application in the industry and research field such as in optoelectronic material such as solar cell, gas sensor, photocatalysis and ultraviolet detector [8]. Graphene is described as a flat single layer of carbon atoms, which the carbon atoms arranged in two-dimensional (2D) honeycomb crystal lattice form. Synthesis of GO have gone through several evolution. Nowadays, Hummers' method is the most common method used in preparing GO. Preparation of GO can be divided into three main method which are Hummers' method, improved Hummers' method and modified Hummers' method [9]. Among these three method, modified Hummers' method produce high yield than other method. Gao et al. reported the fabrication of a U-bent optical fiber sensor for ethanol aqueous concentration detection ranging from 5% to 100% [10].

The result shows U-bent fiber coated with GO has higher sensitivity and more distinguishable compared to bare U-bent fiber. Therefore, in the study the concentration limit obtained were 5%. In addition, Azad et al. reported the fabrication of tapered silica optical fiber coated with ZnO nanorod for detection of ethanol concentration. The detection of ZnO coated nanorod tested with ethanol with different concentration ranging from 20% to 80% [11]. In reference to this matter, this research study proposed a plastic optical sensor coated with ZnO and GO for ethanol detection.

## 2. Materials and methods

### 2.1. Preparation of ZnO thin film

ZnO film is prepared by using sol-gel immersion method [6]. To prepare the solution, 0.35 M of zinc nitrate hexahydrate and HMTA is dissolved in 100 ml of deionized water. The glass substrate is immersed in the solution and placed in the oven for 5 hours with temperature of 75 °C. After 5 hours, rinse the coated glass substrate with deionized water and dried the sample by using hot plate. The solution is then stirred for 2 hours until it dissolved completely. In order to investigate the crystallographic structure of prepared sample, ZnO nanorod was examined under Bruker D8 Advance X-ray diffractometer by using $CuK_\alpha$ wavelength (k = 1.5406 Å) in 2θ range of 30° until 60°. The surface morphology of ZnO film were observed through FESEM (GeminiSEM 500-70-22). The synthesis of GO is done via modified Hummers' method where we already reported in our previous study with their characterisation [12].

### 2.2. Modified POF sensor

The cladding of the fiber is removed by using chemical etching process. The cladding is made from fluorinated polymer and core is made from polymethyl-methacrylate resin with refractive index of 1.40 and 1.49, respectively. The optimum parameter of unclad POF fiber as a sensing medium is 3 cm in length and 0.5 mm waist diameter at the middle of the fiber [13]. The unclad POF was immersed in the 100% of pure acetone solution until it reached 0.5 mm waist diameter. The surface became rough due to interaction between fiber's cladding and acetone. The fiber is immersed in deionized water in order to stop the reaction with acetone. Then, ZnO film will be coated onto the etched fiber by using drop casting technique. For experimental setup, optical light source with wavelength of 650 nm and optical power meter is connected at the both end of coated POF fiber as shown in Fig. 1. For analyte preparations, absolute ethanol was dilute in deionized water according to the concentration ranging from 0.5% to 3.5%, respectively.

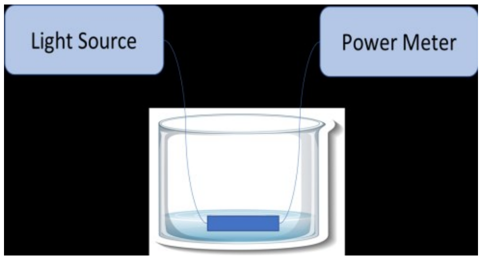



*Fig. 1. Experimental setup of unclad fiber in ethanol solution*

## 3. Results and discussion

### 3.1. Characterization of nanomaterials

The structural properties of ZnO film is determined by using XRD spectra as shown in Fig. 2. The diffraction patterns revealed that the prepared ZnO film was a well indexes to hexagonal wurtzite structure [7]. The high diffraction peak intensity found at planes (100), (002) and (101) and another two low peak intensity at planes (102) and (110). The crystallite size for plane (100), (002) and (101) is 47.685 nm, 30.964 and 46.091 as summarized in Table 1. The peak at the plane (002) have a low intensity [14] that due to the low tendency of ZnO to grow along the *c*-axis or vertically on the glass substrate. Most of the ZnO nanorods growth horizontally as shown in FESEM image in Fig. 3. The growth condition can be related to the absence of ZnO seed particle that acts as nucleation based for nanorod particle to growth [15].

*Table 1. Summary of crystal structure parameter of ZnO nanorods*

| Planes | 2θ (°) | FWHM (°) | D (nm) |
|---|---|---|---|
| **(100)** | 31.091 | 0.174 | 47.685 |
| **(002)** | 34.346 | 0.268 | 30.964 |
| **(101)** | 35.287 | 0.180 | 46.091 |
| **(102)** | 46.761 | 0.040 | 207.479 |
| **(110)** | 54.716 | 0.040 | 207.481 |

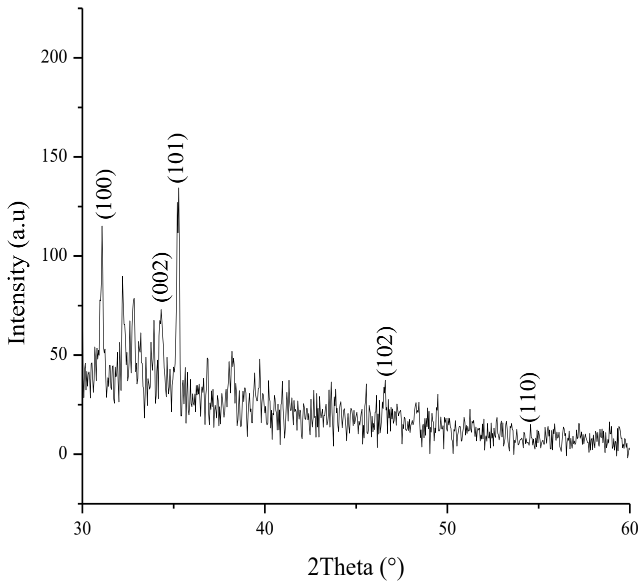
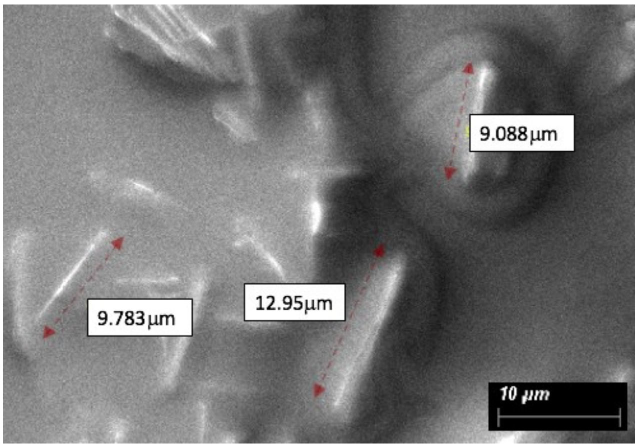
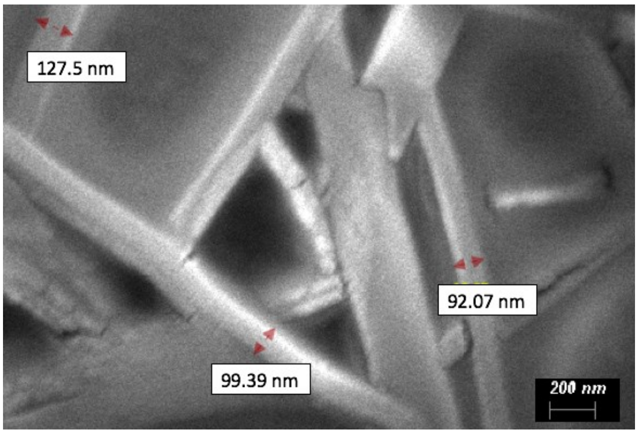



*Fig. 2. XRD spectra of prepared ZnO nanorod*

Fig. 3 show the morphology of ZnO film with magnification of 1 kX and 20 kX. ZnO growth uniformly on the surface of the glass substrate. ZnO nanorod stack to one another in a small group forming many groups disperse on the surface of the substrate. It shows that ZnO nanorods shape as fibrous stacked with each other horizontally. The length of selected nanorods around 10 µm in average with a diameter of 127.5 nm, 99.39 nm and 92.7 nm. The FESEM and raman spectroscopy already been study by our previous study where GO has a layer folded and overlapping to each others and continuous at the same time [12].




(a)




(b)

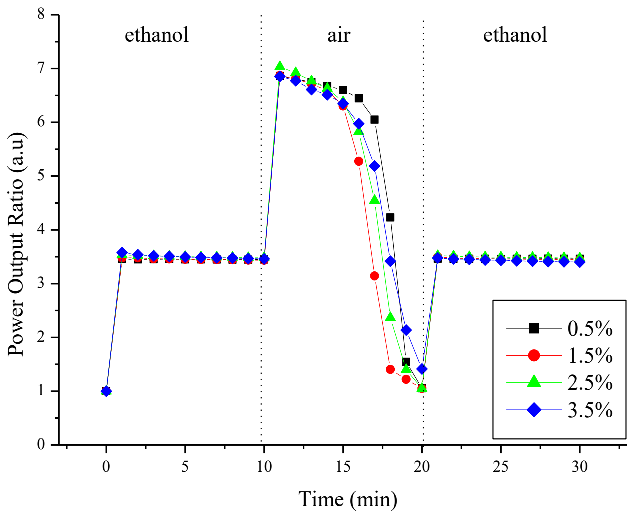
*Fig. 3. FESEM images of ZnO nanorod with magnification of (a) 1 kX and (b) 20 kX*

### 3.2. Ethanol sensing

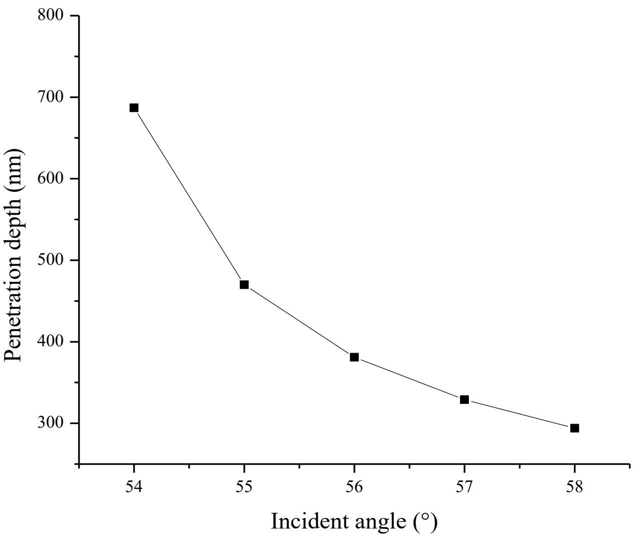
Fig. 4(a) shows the response and recovery time of ZnO coated POF towards 0.5%, 1.5%, 2.5% and 3.5% of ethanol concentrations. When the fiber is exposed with ethanol solution, the power output ratio increased until it reach saturated point in the first minute. Meanwhile, for recovery properties, the output signals increase abruptly at minutes 11 before the signal decrease gradually and reach the based value. This phenomenon is due to the osmosis effect occurs from the existence of solute in the water. This effect continues until a balanced condition achieved and continue to sense normally [16]. Fig. 4(b) shows penetration depth of ZnO coated fiber. The magnitude of the penetration depth, $d_p$ of the evanescent wave can be measured by using equation (1),

$$d_p = \frac{\lambda}{2\pi\sqrt{(n_1^2 \sin^2\theta - n_2^2)}} \quad (1)$$

where $\lambda$ is the wavelength of light source, $\theta$ is the angle of incidence to the normal at the interface and $n_1$ as well as $n_2$ are the refractive indices of denser and rarer media, respectively. The value decrease with the increasing of incident angles at medium B where light incident at coated material and air interface as shown in Fig. 5. This shows that less light loss to surrounding medium as incident angle increase. Since value of incident angle is larger than critical angle and therefore total internal reflection occur at medium B. The refractive index of ZnO nanorod coated onto the POF surface changed lead to the backscattering light into the core [17].




(a)




(b)

*Fig. 4. (a) Response and recovery and (b) Penetration depth value for ZnO coated POF (color online)*

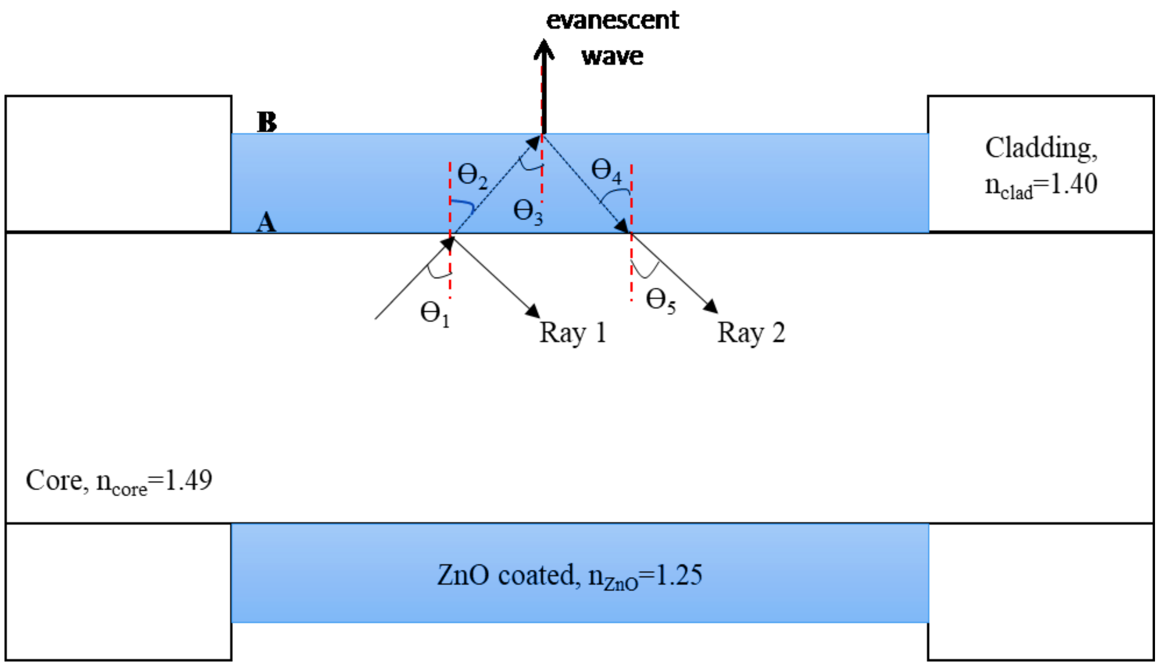



*Fig. 5. Schematic of fiber's mechanisms (color online)*

Meanwhile, Fig. 6 (a) shows response and recovery and time of GO coated POF sensor. It shows a distinct power output ratio response toward different ethanol concentration. In addition, the power output ratio increases as the concentration increase due to the increasing in refractive index. In term of recovery, different concentration gave different recovery times. Concentration of 3.5% took the longest time recovery due to the highest number of ethanol molecule attach on the POF surface compare to other concentration. For GO coated fiber, when ethanol molecule interact with GO films, the GO film will swell since the presence of carboxyl groups at the edge of GO nanosheets [18]. GO captured the ethanol molecules, the refractive index of GO is higher compared to ethanol solutions [10]. Gao et al. produced an ethanol sensor with limit of detection 5% by using U-bent optical fiber sensor [10]. The loss in Fiber coated ZnO is higher compared to GO, so higher loss is predicted for ZnO coated POF. Fig. 7 shows the sensitivity of GO coated POF sensor tested in different concentration values. The sensitivity of this sensor is 0.2361 a.u/% with slope linearity of 89% and limit of detection 1.29%. As a result, GO coated POF is selected for Beer testing.

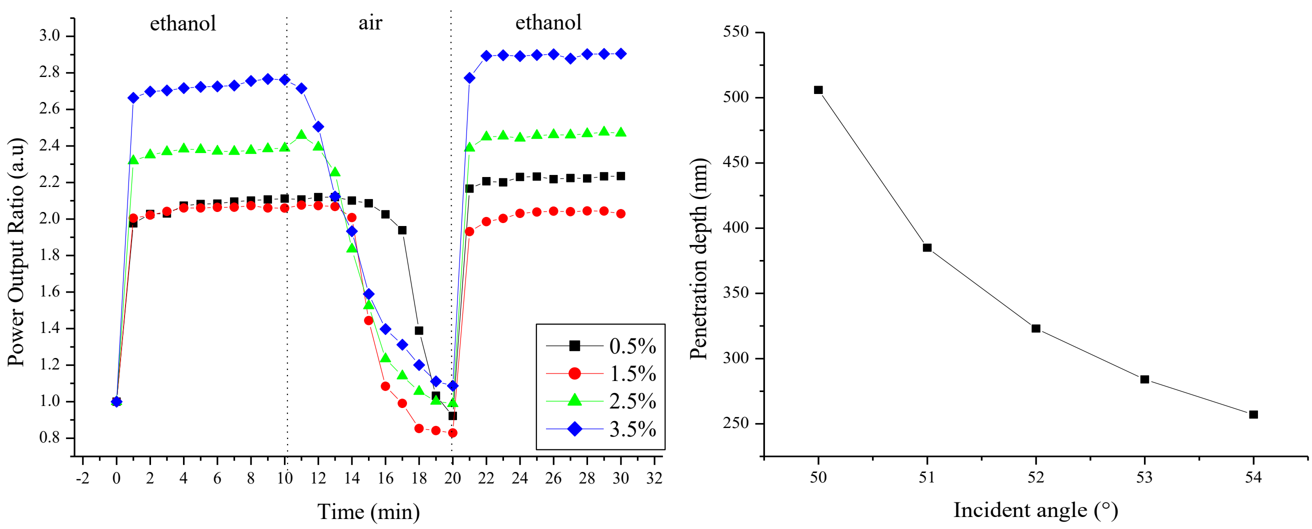



*Fig. 6. (a) Response and recovery for GO coated POF and (b) Penetration depth value (color online)*

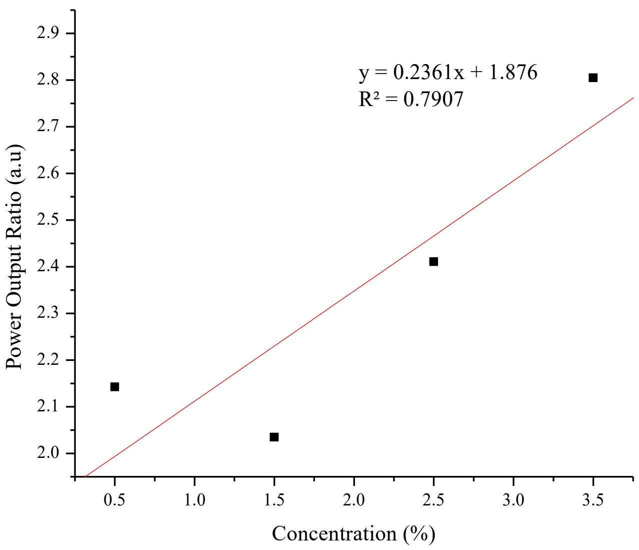



*Fig. 7. Sensitivity value of GO coated POF*

### 3.3. Beer sensing of GO coated POF

In the previous section, GO coated fiber shows higher sensitivity performance toward different ethanol concentration compared to ZnO coated fiber with 0.2361 a.u/% with slope linearity of 89%. Limitation of detection of this sensor is 1.29% and the result presented by the following function of GO coated POF with different concentration ethanol shown in equation (2).

$$y = 0.2349\% + 1.8160 \quad (2)$$

Therefore, to study the feasibility of the sensor toward real sample, GO coated POF was tested with 2% alcohol content Beer available in the market. Fig. 8 shows the power output ratio measurement as function of time when GO coated POF tested with Beer sample. The respond and repeatability time of this sensor is 10 minutes respectively. However, this sensor took 35 minutes to recover to its initial value. This may due to the other substance that binds on the surface of GO since the beer contain several flavor concentration. After the calculation, it is found that the value obtained was 5.57%.

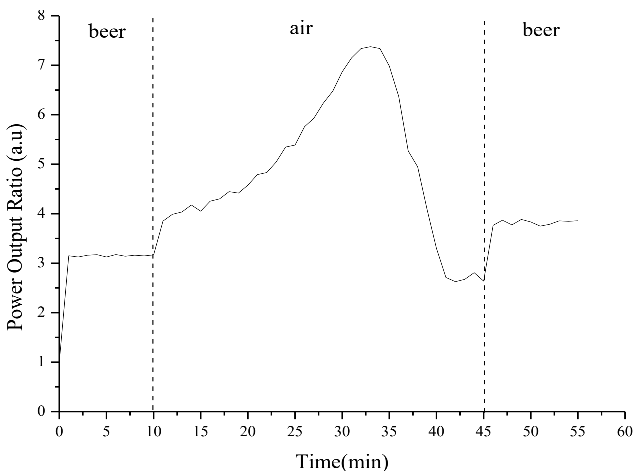



*Fig. 8. Detection of 2% alcohol content beer with POF coated GO*

## 4. Conclusion

In conclusion, ZnO and GO coated POF had been successfully fabricated and briefly discussed in this paper. The optimum condition for unclad POF sensor without coating is when the waist diameter is 0.5 mm with unclad length of 3 cm when detected in various concentration of ethanol solution. The sensitivity obtained by GO coated POF is 0.2361 a.u/% with slope linearity of 89%. GO coated POF shows optimum performance of POF sensor regarding of its limit of detection and interaction between ethanol molecules. Therefore, this sensor is used in the application section where the sensor is tested with real sample of beer contains 2% alcohol concentration as claimed by the manufacture. After doing some calculation, this sensor detect the concentration of the beer as 5.57%. This high value obtained may be due to the presence of high concentration of other ingredient such as lemon concentrated and others. For the future suggestion, the molarity of GO samples can be varied in order to examine the effect of concentration on fiber's sensitivity. The high number of samples will provide more accurate results and display a good detection pattern.

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