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PMMA Doped Multi Walled Carbon Nanotube (MWCNTs) Microfiber for Alcohol Sensing Application

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ABSTRACT

PMMA polymer microfiber doped Multi Walled Carbon Nanotubes (MWCNTs) was reported for alcohol sensing application. The sensitivity of the sensor is increasing relatively with the increment of the alcohol concentration which affects the transmission output power. However, the challenges are on choosing the right material and the simplicity on the fabrication of microfiber sensor for an improvement of the sensitivity of the sensor. A PMMA polymer microfiber doped MWCNTs was introduced for an application of alcohol detection system. Direct drawing technique was used to form a uniform waist size of microfiber sensor with 6μm diameter and 5mm length respectively. The performance of the fabricated sensor was tested with two types of alcohol, namely ethanol and 2-propanol at concentrations varying from 2% to 8% with 2% intervals. The performance which includes sensitivity, linearity and resolution were studied and analysed for the undoped PMMA and PMMA doped MWCNTs-doped polymer microfiber. The PMMA doped MWCNTs sensor which exhibited higher sensitivity for ethanol sensing with 83.23dBm/% with a linearity of 99.96% and a sensitivity of 73.75dBm/% with linearity 99.82% for 2-propanol sensing. The resolution has improved significantly by 0.0004% and 0.0007% respectively. In conclusion, PMMA doped MWCNTs was able to increase the sensitivity as well as the reproducibility of the microfiber sensor for the alcohol detection system.

Keywords: *polymer; microfiber; alcohol sensor; MWCNTs; PMMA.*

1. INTRODUCTION

Alcohol was widely utilized over the years in the food enterprise, biotechnology and medicinal drug wherein an analysis of alcohol is crucial in justification of its toxicological and psychological impact. Ethanol, methanol (or methyl alcohol) and isopropyl alcohol are perhaps the three most commonly used alcohol. The method commonly used for its concentration determination based on chromatographic techniques has a lot of disadvantages in terms of requiring expensive instrumentation; low stability and long analysis time such gas chromatography, high performance liquid chromatography (HPLC) and capillary electrophoresis. Similarly, there are other techniques such as Raman spectrometry, enzymatic method and colorimetric method. Microfiber sensors' attractive features such as immunity to electromagnetic interference, the possibility for spectral multiplexing, lightweight and cost effective received a tremendous amount of interest to be used as one of the alternative method for ethanol sensing [1].

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In recent times, the current trends of fiber optics sensor with spatial miniaturization has become a requirement for higher performance and versatilities on optical sensors due to the increasing demand along with the rapid progress in micro/nanotechnology. Notably, microfiber sensor is one of the best candidates due to its faster response, higher sensitivity, low power consumption and better spatial resolution by reducing the size of a sensing structure [2]. Conducting polymers including polyaniline (PAni), polypyrrole (PPy) and polythiophine (PTh) discovered by Heeger in 1960 are being used as a detection medium in fiber optic sensors because of the uncommon assets of processing high electric conductivity and displaying a number application from semiconductor to close to-metallic behaviour. Moreover, they also display the optical properties of metals or semi-conductors [3]. Other functionalized polymers also have been proposed as a microfiber sensor such as polyacrylamide (PAM), polyaniline (PAni), poly vinyl alcohol (PVA), poly ethylene oxide (PEO), polystyrene (PS) as well as Poly Methyl Methacrylate (PMMA). Masayuki Morisawa et al. [4] reported an integrated plastic optical fiber (POF) ethanol sensor with swelling polymer by using Novolac resin. However, the result shows the sensor failed with ethanol solution with lower concentration below 10v/v%. Chiam et al. [3] demonstrated a microfiber sensor coated with PAni as a device to come across diverse alcohols, specifically methanol, ethanol, 1-propanol and 2-propanol at different concentrations. The results give a red shift in the output spectrum with an increasing steric impact, thus increasing the dihedral angle and band gap energy with the presence of PAni.

PMMA which is commonly known as acrylic glass or simply acrylic in the market with optically clear (transparent) thermoplastic was discovered by British chemists, Rowland Hill and John Crawford in the early 1930s, followed by its first application by a German chemist, Otto Rohm, in 1934 [5]. PMMA has many fascinating properties such as high impact strength, is lightweight, shatter-resistant, and exhibits favourable processing conditions and has a wide range of application especially those areas that require transparency and light transfer, high durability and good water resistance. The recent developments of PMMA were revealed in molecular separation, pneumatic actuation, viscosity, biomedical, solar, nanotechnology, polymer conductivity, optical and sensor [5]. Ninik Irawati et al. [6] experimentally demonstrated a new relative humidity sensor based on the PMMA microfiber doped agarose gel in 2016. The microfiber sensor doped agarose gel are said to function well within the operation range of 50% to 80% RH and with a sensitivity of 0.1 μW/%, linearity more than 97% and the resolution 0.2% is obtained based on a standard deviation of 0.011μW. The doping of agarose gel was enabled by the use of PMMA as agarose gels are stable, non-water soluble and commonly used in other sensing application. M. Latino et.al [7] demonstrated ethanol sensing properties of PMMA-coated fiber Bragg grating. He stated that the effect on the peak shift caused by the swelling of PMMA layer due to the absorption of ethanol from the gas phase could be related to the ethanol concentration which can be recorded as an extension or compression of the fiber grating.

Carbon Nanotubes (CNT) have been widely studied over the last two decades by many research due to its great potential in different fields. These include applications in the field of nanotechnology, nano medicine, transistor, actuators, sensor, membranes and capacitors. In fact, CNTs have many good properties such as light weight, small size with high aspect ratio, good tensile strength, and good conducting characteristic [8]. Wong et al. [9] were the first to establish its possibility to sense functional chemical groups attached onto the ends of CNTs. From the studies, various types of sensors with high sensitivity to gases containing nanotube

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composite pellets were constructed to observe leaks in chemical plants. Wood et al. [10] noted that CNTs are very sensitive to liquid immersion or polymer-embedding processes, as the nanotubes slightly deform in the presence of different liquid media.

As a chemical sensor such as alcohol detection system, the material used should be able to respond to the changes of the concentration of the liquid or in gaseous media. A good chemical sensor should have good electrical properties, high sensitivity to charge transfer, the chemical doping effect of various molecules, and be capable of immobilization [11]. Therefore, taking into consideration the qualities of the materials for the chemical sensors, a CNT and PMMA composite or modified CNT would be a very good material for chemical sensors. PMMA is the polymer that would enhance the behaviour at the interface between the carbon nanotube and the copolymer [12].

Thus, a high sensitivity of the alcohol sensor can be achieved without having to implement tedious physiochemical analysis in the lab. In addition, accurate, inexpensive and in-situ analyses can be implemented using sensitive optical sensors based on PMMA doping with MWCNTs. To emphasize, this research mainly focuses on the development of a fiber sensor to detect the alcohol at different concentrations. The objectives are to construct and demonstrate a PMMA microfiber-based alcohol detection system by using a silica-PMMA-silica microfibers cascading technique and to investigate the performance of the PMMA doped MWCNTs microfiber as an alcohol sensor.

2. METHODOLOGY

2.1 Preparation of Tapered Fiber

The preparation of the alcohol detection system starts with the biconical tapered fiber where a silica fiber was connected to the single mode fiber (SMF) pigtail at both ends by using fusion splicing. The splicing loss was achieved with a 0.01 dB loss. Next, the buffer coating of the silica fiber (SMF corning 28) was removed from the taper region with a length of 1.5cm and cleaned with alcohol. Figure 1 indicates a schematic illustration of the silica microfiber fabrication setup in order to reduce the diameter of the heated silica when it is stretched by using two fiber mount through the use of an oxy-butane burner as a torch where the flame is produced from oxygen and butane.

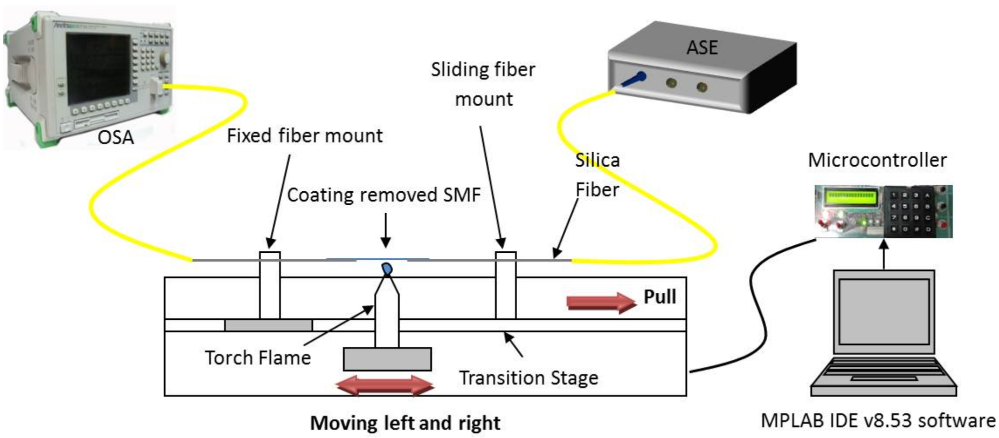

Figure 1: Schematic Illustration of the Silica Microfiber Fiber Setup by Using Flame Brushing Techniques

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This flame brushing technique is most commonly used due to its high flexibility in controlling the flame movement, fiber stretching length and speed. This technique is not only able to fabricate the silica microfiber with good accuracy but also creates an evanescent field around decreased microfiber diameter which later will be a bridge for the microfiber sensor. A measured tapered waist diameter of up to 8 µm was achieved, as shown in Figure 2.

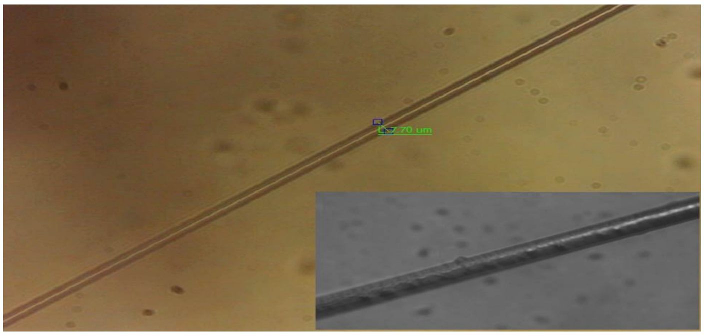

Figure 2: Microscope Image with 20x Magnification of the Tapered Fiber

2.2 The Fabrication of the PMMA Doped MWCNTs

Direct drawing technique was applied in the fabrication of the PMMA doped MWCNTSs microfiber. First, PMMA with a refractive index of 1.49 is dissolved in 5ml acetone to form a homogenous solution. Afterwards, 0.1g of the MWCNTs was added to the PMMA solution with the ratio mixture of PMMA: MWCNTs = 1g: 0.1g. The MWCNTs used was in the form of MWCNTs- acrylonitrile butadiene styrene (ABS) based fused deposition modelling (FDM) 3D printer filament thus for this reason acetone was used to dissolve the ABS in order to produce MWCNTs-acetone suspension [13]. Furthermore, the easier the solvent can evaporate; less solvent will remain to affect the curing reaction [14].

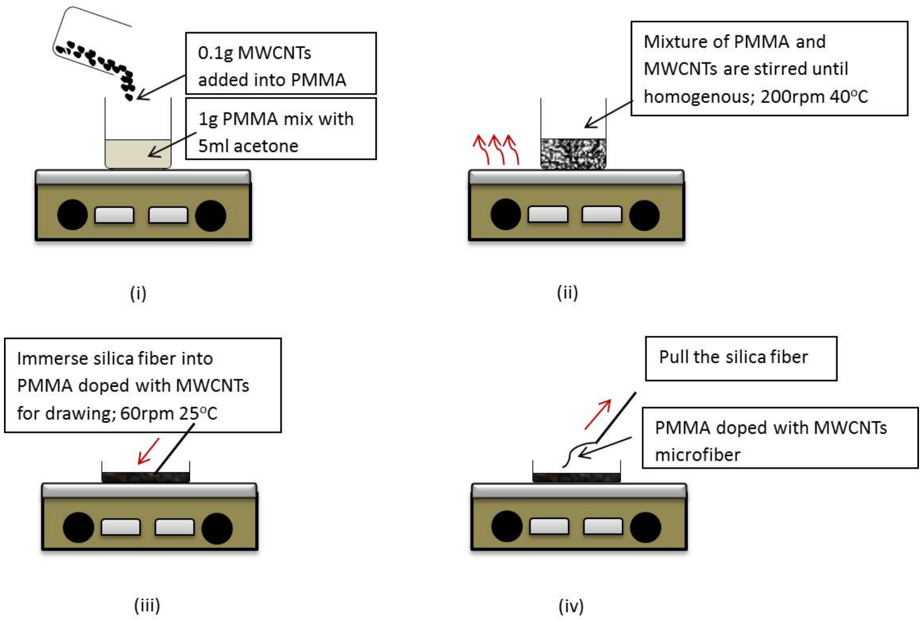

Figure 3: Schematic Illustration of PMMA Doped MWCNTs Microfiber Fabrication Process

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Schematic illustration shown in Figure 3(i) shows the solution was stirred by using the Corning PC-420D Stirring Hot Plate at 200rpm and the temperature was maintained at 40°C where the stirrer process took about 1 hour and 45 minutes until a homogeneous mixture was achieved. Then the homogeneous mixture of the PMMA doped MWCNTs was placed in a hot plate disc and was stirred again at 60 rpm and the temperature was maintained at 25°C until a suitable viscosity was formed. Once the desired viscosity was achieved, the tip of a silica fiber was immersed into the solution and the extended PMMA doped MWCNTs microfiber was quickly quenched in air with at speed 0.1 - 1m/s [10], forming a microfiber with a uniform waist diameter of 6µm and a length of up to 5mm as shown in Figure 4. The temperature of the hot plate was kept constant at 25°C during the direct drawing process. The PMMA doped MWCNTs microfibers made via this approach are uniform in diameter over an extended length with practical flexibility [6].

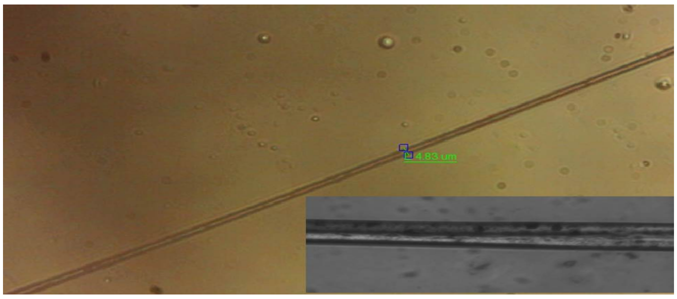

Figure 4: Microscope Image with a 20x Magnification of the PMMA Doped MWCNTs

2.3 Experimental Setup for the Alcohol Sensor Based on PMMA Doped MWCNTs

The alcohol detection system as illustrated in Figure 5 below was setup where an Amplified Spontaneous Emission (ASE) with a wavelength of 1550nm was used as a light source and the optical property of the PMMA doped MWCNTs towards different types of alcohol was analysed by using an Optical Spectrum Analyser Anritsu MS9710C (OSA). The experiment was operated under regular lab condition at the room temperature of 27±3°C with a relative humidity of 45±5%. First, a tapered silica microfiber that was fabricated by using flame brushing technique was used to hold the polymer microfiber. In order to reduce any mechanical vibration that might affect the transmission output power, the experiment setup was done on a vibration-free table. Next, a small gap of about 1mm was created by cutting the silica-tapered fiber in the middle. Then, the PMMA doped MWCNTs microfiber with a length of up to 5mm and silica microfibers were attached electrostatically by allowing them to overlap with the two ends of the polymer microfiber. The polymer and silica microfiber can be easily maintained due to the high level of diameter uniformity and surface smoothness of the fabricated microfibers. Most molecules located at the surfaces of the microfibers can contact firmly when adhered together which produce strong electrostatic forces namely Van der Waals force at the joint area [6, 15]. This electrostatic force enables light to propagate through the polymer microfiber and transmitted to OSA. To enhance the bonding between the microfiber sensor and the tapered fiber, DuPont™ Teflon® AF Amorphous Fluoropolymer was used as glue at both ends of the microfiber sensor and exposed under UV light for 10 minutes.

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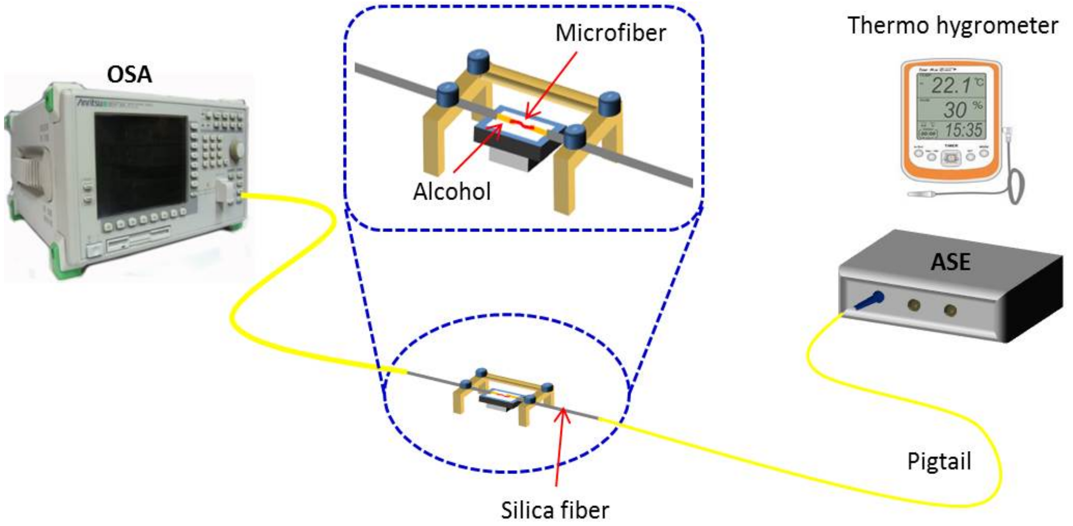

Figure 5: Experimental Setup for the Measurement of Alcohol Concentration Using a PMMA Doped MWCNTs Microfiber

Finally, a small dish filled with 10 ml of alcohol solution was placed under the microfiber sensor. The environment was controlled and kept persistent within 45±5% and monitored by using a thermo-hygrometer during the process. The microfiber sensor was left for 2 minutes in order to return to the initial value before testing it with the other alcohol. The output changes were recorded after the spectrum stabilized.

3. RESULTS AND DISCUSSION

The output spectra between the undoped PMMA and PMMA doped MWCNTs are shown in Figure 6 where the output power has dropped from -38.17dBm to -50.34 dBm due to the changes of the material after PMMA was doped with MWCNTs. By doping with MWCNTs, the microfiber sensor became more sensitive to the surrounding because of the alteration of the refractive index and the presence of high evanescent field [4-6].

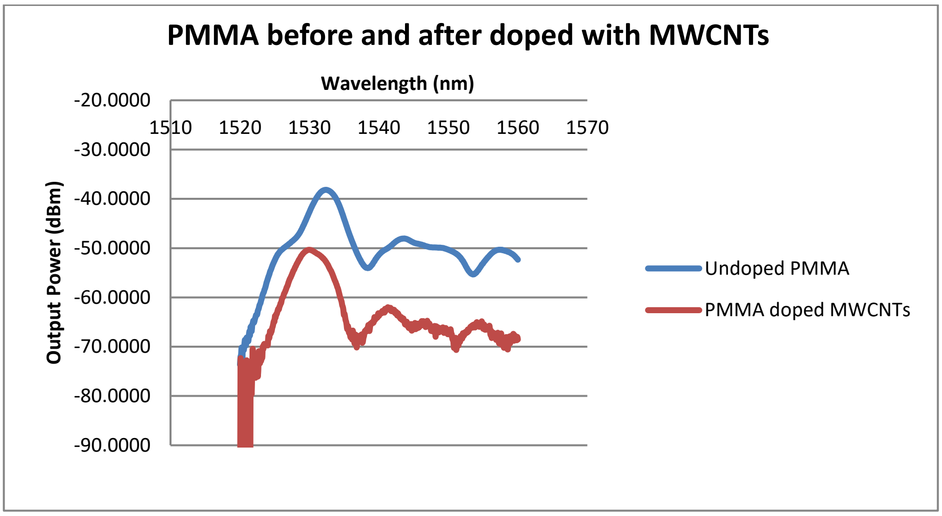

Figure 6: Output Power of PMMA Before and After Being Doped with MWCNTs

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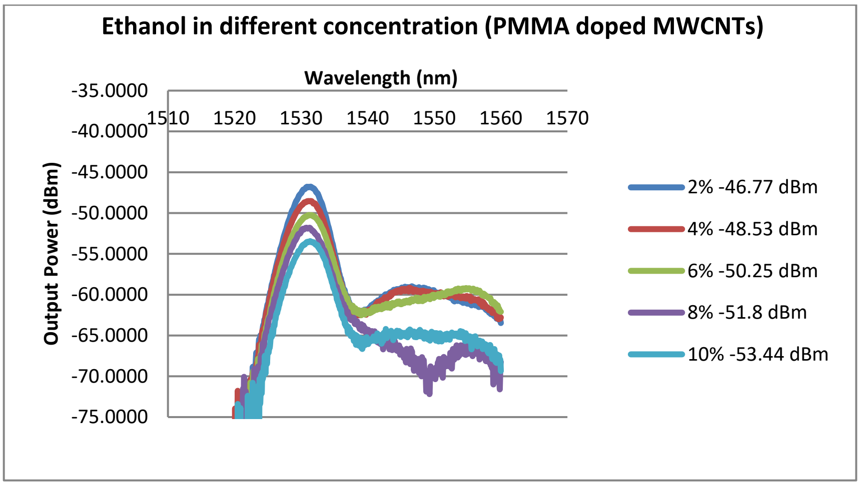
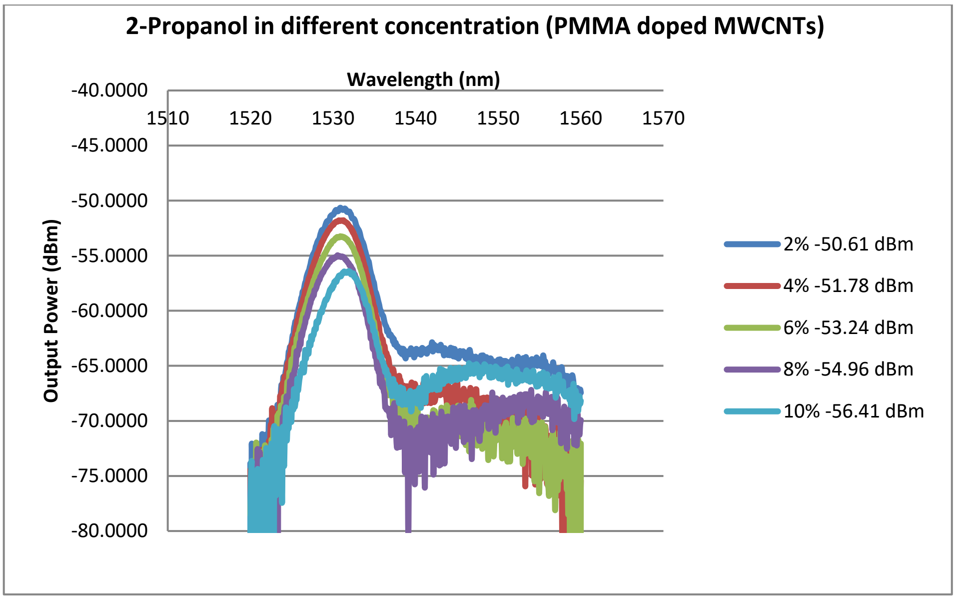
The proposed sensor was tested with two types of alcohol, namely ethanol and 2-propanol at different concentrations at the same experimental and controlled environment conditions as depicted in Figure 7. As the concentration increases the output spectrum reduces proportionally due to the different refractive index in the solution and the effective refractive index at the proposed sensor as doping materials in the polymer microfiber can affect the performance of the optical microfiber sensor. Based on the output spectrum, Ethanol has the highest transmission output power compared to 2-proponal for all concentrations. The output spectra show that as the concentration increases from 2% to 10%, the transmission output power reduces from -46.77dBm to -53.44dBm.



(a)



(b)

Figure 7: Power Output Spectrum at Different Alcohol Concentration (a) Ethanol (b) 2-Propanol

Similarly, the output spectrum for 2-propanol shows a reduction in the output power from -50.61dBm to -56.41dBm as illustrated in Figure 7(b). The ability of the proposed sensor to

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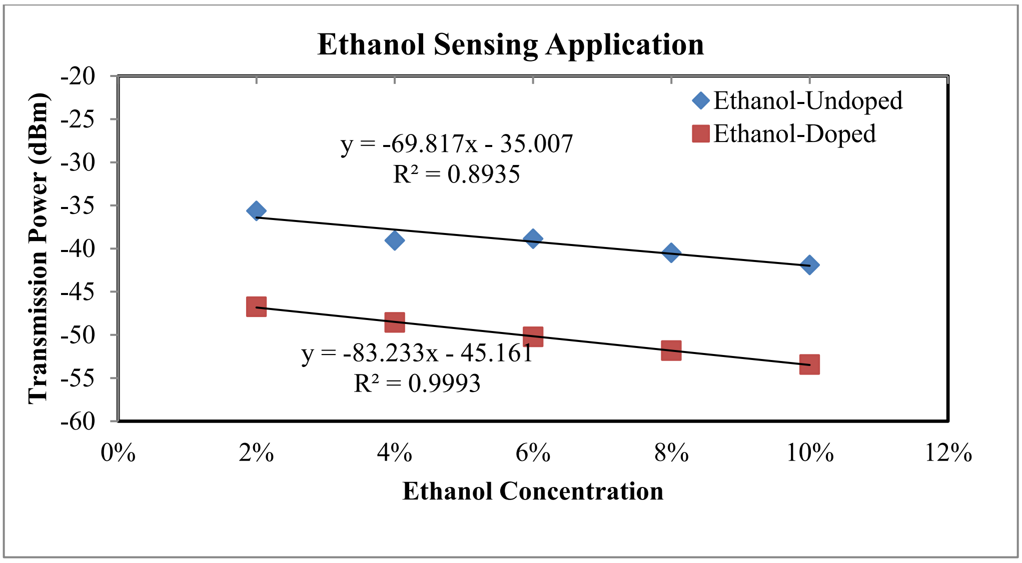
produce different output spectrums in response to different kinds of alcohol indicates its capability to sense different kinds of alcohols.



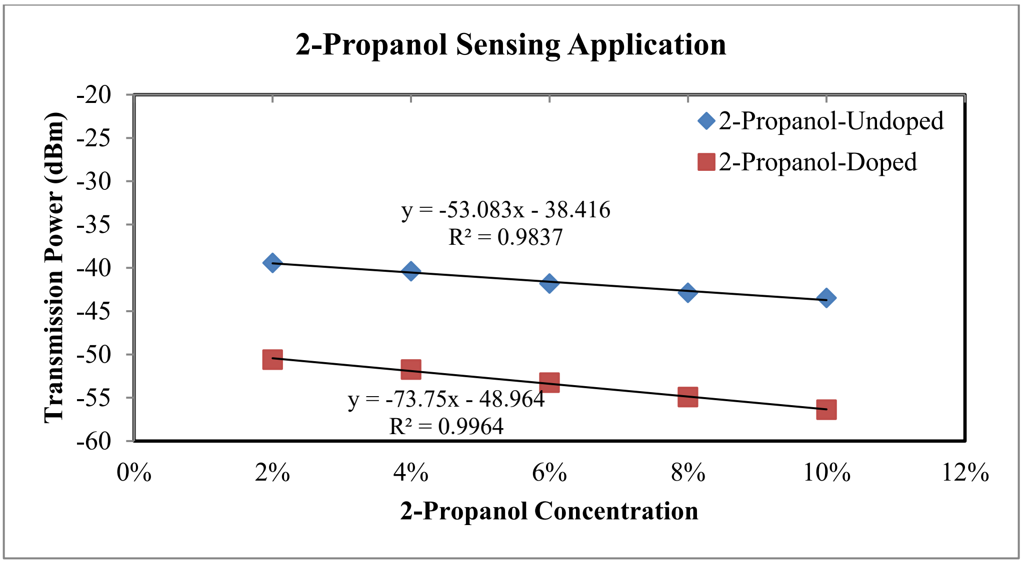


Figure 8: Transmission Output Power for the Detection of Various Kinds of Alcohols at Different Concentration for the Undoped PMMA and PMMA Doped MWCNTs

The performances of the proposed sensor are investigated based on its sensitivity, linearity and resolution as an alcohol sensor. The sensitivity of the PMMA doped MWCNTs for ethanol sensing has a large and constant sensitivity of 83.23dBm/% in its operating range as plotted in Figure 8 compared to the undoped PMMA with a sensitivity of 69.82dBm/%. Equally for 2-propanol alcohol, the sensitivity has significantly increased from 53.08dBm/% to 73.75dBm/%. Furthermore, it is observed that the linear trend line for the undoped PMMA and PMMA doped MWCNTs are almost similar with a slope linearity of more than 99% when it was immersed with ethanol and 2-propanol. As can be seen ethanol has advancement in linearity slope by 5.43% after PMMA doped with MWCNTs. In addition, the resolution of

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the detection is measured by dividing the standard deviation with the sensitivity which defines the smallest detectable change of the proposed sensor. The calculated resolution for ethanol offered an enhancement from 0.0028% for the undoped PMMA to 0.0004% after doped with MWCNTs. Meanwhile, 2-propanol also results in a great resolution with 0.0007% which is less than 0.0029% for the undoped PMMA.

The overall performance of the undoped PMMA and doped MWCNTs-PMMA alcohol sensor is summarized in Table 1 where the PMMA doped MWCNTs sensor produced a higher sensitivity for ethanol of 83.23dBm/% with a linearity of 99.96% and 73.75dBm/% with linearity 99.82% respectively when immersed with 2-propanol.

Table 1: Comparison of the Performances Between the Undoped PMMA and PMMA Doped MWCNTs Microfiber Sensor

Parameter	Unit	Ethanol (undoped)	Ethanol (doped)	2-Propanol (undoped)	2-Propanol (doped)
Sensitivity	dBm/%	69.817	83.233	53.083	73.750
Std Deviation	dBm	0.1952	0.0361	0.1518	0.0551
Resolution	%	0.0028	0.0004	0.0029	0.0007
Linearity	%	94.53%	99.96%	99.18%	99.82%
Limit of Detection	%	0.0143	0.0120	0.0188	0.0136

In addition, the standard deviation for ethanol sensing was reduced by 82%, and 2-propanol by 64% compared to the undoped PMMA which results in the improvement of the stability of the measurement taken. The resolution of the PMMA doped MWCNTs sensor also has improved where the resolution is lower for ethanol and 2-propanol with 0.0004% and 0.0007% respectively which indicates the minimal change of the measure and that can be used for detection. Above all, the undoped PMMA and PMMA doped MWCNTs sensor produce practically the same linearity slope for the alcohol tested with more than 99% with an improved linearity slope of 5.43% for ethanol. The detection limit is calculated by dividing the resolution with the sensitivity in order to determine the efficiency and performance of the system. Ethanol has a limit of detection of 0.012% and 0.014% for 2-propanol which is lower than the undoped PMMA. The lower limit of detection indicates the higher efficiency and better performance of the PMMA doped MWCNTs microfiber alcohol sensor.

4. CONCLUSION

As a conclusion, a simple alcohol optical sensor utilizing PMMA microfiber doped MWCNTs is developed using a silica-PMMA-silica microfiber cascading technique. The refractive index of the fabricated microfiber sensor changes during the fabrication process and thus decreases the transmission of light through the proposed sensor. The transmission output power decreases proportionally as the concentration of alcohol increases from 2% to 10%. As a result, the proposed sensor gives a higher efficiency in terms of its sensitivity, repeatability, linearity, and resolution in detecting various alcohol concentrations, namely ethanol and 2-propanol.

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