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Abstract. The width of spiral-patterned zinc oxide (ZnO) nanorod coatings on plastic optical fiber (POF) was optimized theoretically for light-side coupling and found to be 5 mm. Structured ZnO nanorods were grown on large core POFs for the purpose of alcohol vapor sensing. The aim of the spiral patterns was to enhance signal transmission by reduction of the effective ZnO growth area, thereby minimizing light leakage due to backscattering. The sensing mechanism utilized changes in the output signal due to adsorption of methanol, ethanol, and isopropanol vapors. Three spectral bands consisting of red (620 to 750 nm), green (495 to 570 nm), and blue (450 to 495 nm) were applied in measurements. The range of relative intensity modulation (RIM) was determined to be for concentrations between 25 to 300 ppm. Methanol presented the strongest response compared to ethanol and isopropanol in all three spectral channels. With regard to alcohol detection RIM by spectral band, the green channel demonstrated the highest RIM values followed by the blue and red channels, respectively. © 2016 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: 10.1117/1.JNP.10.036009]

Keywords: zinc oxide; spiral pattern; visible-light wavelength; optical fiber; light-side coupling; nanorods.

Paper 16049 received Mar. 22, 2016; accepted for publication Jul. 18, 2016; published online Aug. 8, 2016.

1 Introduction

A chemical sensor is a device that transforms chemical information in the form of concentration of a specific material into an analytically useful signal.1 A large number of commercially available chemical measurement systems are found in the market today and can be classified by the type of analytical signal required for measurement. For optical-based instrumentation, these include, among others, absorbance,2 luminescence,3 light scattering,4 and fluorescence.5 Due to the simplicity of directing light into a sensing platform, optical fibers have found applications for the measurement of chemicals in food,6–9 security industry safes,10 and clinical materials.11 However, these chemical vapor sensors are usually associated with high-cost, high-operational
power requirements, and complexity in operation. Laser light sources are generally used in optical sensing applications, but costs related to the laser and the mechanical alignment apparatus can be relatively high. Application of laser light sources onto coated fibers also poses several problems. Inequality of beam distribution onto the fiber and small beam diameter can lead to fluctuations, nonrepresentation, and low intensity. In addition, the most common method adopted in optical sensing is based on the quenching of luminescence from a range of chemical species. Most of the luminescent indicators used for chemical sensing suffer from the disadvantages of having both shortwave excitation and small stokes shift, thus adding complexity to the required measurement instrumentation.

In previous work, the authors proposed an approach to overcome these issues using light-side coupling through scattering of zinc oxide (ZnO) nanorods coated on silica multimode optical fibers. ZnO nanorods coated on the fiber contributes into side coupling to the guided modes. However, ZnO nanorods as well causes light to leak outside the core. This can effectively reduce the device’s efficiency and sensitivity. One way to increase the magnitude of light intensity is through the use of a larger plastic optical fiber (POF) core that increases the scattering area. Structuring the growth of ZnO into separate patches allows coupling light from different segments of the POF.

Over the years, the bulk of work on ZnO focused on synthesis and surface modification, treatment, and protection. A variety of structures including one-dimensional nanorods, two-dimensional nanoplates, and three-dimensional nanoflowers have been synthesized. However, patterned growth, the application of a helical pattern with mm dimensions, of ZnO nanorods on cylindrical surfaces with small diameter (e.g., ~2 mm) of a typical optical fiber still remains challenging for optical applications. Practically, unpatterned growth is preferred due to reduced complexity during fabrication and shorter treatment time. As a result for sensing applications, our previous work was initially based on unpatterned growth of ZnO nanorods on the POF core. However, we found that although unpatterned ZnO nanorod layers enhanced optical side coupling with the fiber, significant levels of backscattering prevented the ingress of light into the fiber. Furthermore, ZnO scattering centers provided a pathway for light leakage. Consequently, these two optical loss mechanisms resulted in low intensity of side coupling of light, a condition that is undesirable in optical applications such as in telecommunications, sensing, and measurements. As reported previously, to increase the intensity of side-coupled light, application of patterned coatings of ZnO nanorods on POF cores was proposed to mitigate the level of backscattering and leakage. It is worth mentioning here that across this manuscript and in our previous publications, the term scattering is used to describe the main phenomenon corresponding to side coupling as shown in Fig. 1. Upon recent theoretical study by the authors, another important factor has been observed to actually contribute into coupling light to the guided modes inside POF particularly at large angles $\theta_i$ (near right angles). At angles close to $90^\circ$, light is guided inside the rods and because ZnO nanorods have higher refractive index, $n_2$ compared to the polymer, $n_3$ forming the POF, light at the outlet of the nanorods diverges with wide field of view inside the fiber. Side coupling is obtained for the portion of this diverging light, which is at angles larger than the critical angle $\theta_c$ between the polymer and the polymer.

![Fig. 1](image-url)  
**Fig. 1** Mechanism of light scatters into POF core by ZnO nanorods at angle larger than critical angle.
core and air $n_1$. Although, for simplicity and for the remainder of this manuscript, the term scattering is used to describe the macroscopic effect of light-side coupling.

In this work, optimization of the spiral spacing of ZnO nanorod-coated regions on the fiber was carried out to produce maximal signal intensity. Theoretically, high-intensity light-side coupling is expected between the scattering ZnO layer and the fiber optic if the width of the ZnO spirally patterned coating is optimized. Also, adaptation of the sensor as a multiple optical channel waveguide sensor for detection of alcohols in the visible wavelength domain was studied. Finally, experimental demonstration of the patterned fiber optic as a multiple optical channel sensor for alcohol vapor is shown.

2 Modeling

Here, a first-order model is derived to simulate the impact of millimeter (mm) scale spiral patterns on power leakage due to scattering by ZnO nanorods. In the side coupling mechanism proposed here, ZnO nanorods allow light to couple inside the guiding region (core of POF). ZnO nanorods as well guide the light outside the fiber core with each bounce at the interface. These two counter effects restrict the coupling to an effective area around a region at the beginning of the ZnO coating. This limits the use of this system in multiple channels as well as for application with extended sources. One way to improve the system response is through spreading the effective coupling area of ZnO nanorods across the fiber. This is achieved by introducing patches of nanorods coating. Optimizing the gaps and width of ZnO coating enhances the system response depending on the light source used. More detailed analysis of the scheme was explained in a previous publication. In the analysis, two cases of ZnO nanorod coating on POF core have always been compared: spirally patterned ZnO nanorod coatings in which a light-blocking layer was applied and unpatterned coating in which ZnO nanorods cover the entire surface of the POF uniformly. The two configurations are shown in Fig. 2. The objective was to optimize the width of spiral-patterned ZnO nanorods coating for the purpose of experimental design.

![Fig. 2](image)

Fig. 2 (a) Spiral-patterned coating of ZnO nanorods on POF core and (b) unpatterned coating of ZnO nanorods on POF core.
In the schemes illustrated in Fig. 2, the visible-light source illuminates the upper hemisphere of the coated POF when oriented normal to its surface. The ZnO nanorods scatter light at different directions accordingly and maximum coupled power $P_o$ to core or cladding mode is defined as

$$P_o = \frac{P_{\text{source}}}{2\pi C_{sc}\rho_a} \psi,$$

(1)

where $P_{\text{source}}$ is the power of the source excitation. The constants $C_{sc}$ and $\rho_a$ are the scattering cross section of one rod (m) and rods density (number of nanorods per unit area $N_{\text{rod}}/\mu\text{m}^2$, respectively. The constant, $\psi$ is the portion of the scattered light that couples into the guided modes of the fiber as

$$\psi = \int_{\theta_{c}}^{\pi} p(\theta - \theta_{\text{inc}}) \sin \theta \, d\theta.$$

(2)

The function $p(\theta - \theta_{\text{inc}})$ is the phase function, which is the probability distribution function or the scattered power as a function of the scattering angles $\theta$. The function is assumed to vary linearly with the incident angle $\theta_{\text{inc}}$. This assumption can be justified here as a small range of angles around normal incidence is considered. At larger angles, this model deviates from the actual system. The critical angle $\theta_{c}$ is the one between the core POF and air.

To study the coupling and source distribution effect, the POF surface was divided into segments of width $\Delta z$ shown in Fig. 3(a). The source excitation is assumed constant over the width. At any segment $h$ on the surface of the POF, exposed to a visible-light source, there is an arbitrary intensity profile $P_s(z)$ causes a portion of $\psi \eta P_s(z)$ to couple to the guided modes. In addition to the excitation, a portion of the previously coupled light (coming from segment $P_{h-1}$) adds to the amount of light coming out of segment $h$ as shown in Fig. 3(b). Notice that, in the figure, the coupling coefficient from segment $h$ is indicated as $\eta_z$. The power coupled out of segment $h$ can then be written as

$$P_h = \psi \eta_z P_s + P_{h-1} - (\eta_z P_{h-1}).$$

(3)

In simulations, the length of POF was selected to 100 segments of 1 mm each for a total of 100 mm and $P_{\text{source}}$ is the power of the source excitation that was fixed to 5 for amplitude. Three coating regions of ZnO nanorods were developed to create spiral-patterned coating on the POF and the widths of the ZnO nanorods coating were varied from 1 to 20 segments as shown in Fig. 2(a). Meanwhile, the unpatterned POF was evaluated by varying the ZnO nanorods coating widths.
from 1 to 100 segments, which is fully coated as depicted in Fig. 2(b). These two scheme coatings were analyzed using Eq. (3) by applying finite difference method. In this case, the widths of ZnO nanorods coating were fixed to three segments (3 mm) starting from segment 10 to 12 (first ZnO region), 13 to 38 (uncoated region), 34 to 36 (second ZnO region), 37 to 62 (uncoated region), and 63 to 65 (third ZnO region). For ZnO unpatterned coating, there is only one ZnO region that is also fixed to three segments (10 to 12). The region was coated with ZnO nanorods has the coupling coefficient, $\eta_z$, higher than zero, and $\eta_z$ for uncoated region is equal to zero. Thus, the power for the segment before segment 10 ($P_{9}$) is equal to zero due to the $\eta_z$ is zero. As the portion of light from segment 9, $P_{9}$ is substituted into Eq. (3) to couple to the amount of light of $P_{10}$. The total light at segment 10 is

$$P_{10} = \psi \eta_{z10} P_s + P_9 - (\eta_{z10} P_9) = \psi \eta_{z10} P_s.$$  

The amplitude of $P_{10} = \psi \eta_{z10} P_s$ is coupled to the amount of light in segment 11. Thus, $P_{11}$ can be written as follows:

$$P_{11} = \psi \eta_{z11} P_s + P_{10} - (\eta_{z10} P_{10}).$$

Then, the coupling light in segment 11 is coupled to the light presents inside segment 12, the amplitude of $P_{12}$ is given as

$$P_{12} = \psi \eta_{z12} P_s + P_{11} - (\eta_{z11} P_{11}).$$

In this case, the coupled light from segment 10 to segment 12 is equal to $P_{12} \approx 0.7$, because the width of ZnO nanorods coating has been fixed to three segments. For the unpatterned POF, the coupling light is consistently equal to $P_{12}$ in the uncoated region until reaching the photodector. The consistency of the coupled light occurs due to coupling coefficients from segment 13 to 100, $\eta_{z13}$ to $\eta_{z100}$ are equal to zero in the uncoated region. Thus, the coupling light reached the photodector can be written as

$$P_{13} = \psi \eta_{z13 to 100} P_s + P_{12} - (\eta_{z13 to 100} P_{12}) = P_{12}.$$  

In spiral-patterned POF, this consistency of $P_{12}$ remains steady in the uncoated region (segment 13 to 38) until the second ZnO nanorods region (segment 34 to 36) has another three segments. The amount of $P_{12}$ is coupled again in the first segment of second ZnO nanorods region. The coupled light keeps increasing until the next uncoated region. The effect of spiral-patterned coating on POF leads to a significant improvement of light intensity as depicted in Fig. 4 achieving a level of coupling light of 0.98. In this case, side coupling was obtained to be a factor of 1.4 times better for spiral-patterned coating as opposed to unpatterned continuous coatings.

It is worth mentioning that the coupled power is normalized to the optical power incident at each segment. Also off-axis, coupling azimuthal modes (or skew rays) are dominantly coupled. These, however, might not be the only modes to be excited in side coupling as radial modes can

![Fig. 4](image-url) The scheme of light propagation for unpatterned continuous and spiral-patterned coating, where ZnO coating region was fixed to three segments (3 mm).
be excited as well. This is due to the main fact that mode excitation happens due to matching the momentum of the scattered light to the propagation constant of guided mode. In general, the assumption of specific power distribution among any set of modes (in any form) with the proposed first-order model especially when large core fiber is used would not have a significant effect on the driven results or the measurement as we estimate the leak due to surface scattering.

3 Experimental

3.1 Fiber Preparation, Zinc Oxide Nanorod Synthesis, and Characterization

Following the previously optimized POF fiber spiral patterning and ZnO nanorod seeding and synthesis procedures, ZnO nanorods were grown using hydrothermal method. Here, standard polymethyl methacrylate (SK-80 POF fibers from Mitsubishi Rayon Co., Ltd, Japan) were utilized in experiments to serve as controls and the same fibers were modified to obtain spiral-patterned POF with a specified spiral pitch angle, spacing, and width. The jacket of the POF were mechanically stripped to expose the core fiber over a length of 10 cm. Figure 5 illustrates the ZnO coating schemes; three widths were varied from 3, 5, to 7 mm for the spiral-patterned and unpatterned POF. These width coatings were selected from modeling result in Fig. 8 due to the significant output differences occurred at small width of ZnO coatings. A fully coated POF (100 mm) was also fabricated to complete the validation. Tape-patterned and unpatterned POFs were then placed in a ZnO seed solution and subsequently into the growth solution to form ZnO nanorods. Percent surface coverage and nanorod orientation were evaluated as described in previous work by evaluation of scanning electron micrographs recorded by a Hitachi, 3400 N system operating at 20 kV.

3.2 Optimization

Optimization of optical input through the POF waveguides was realized by correlation with maximal values of the output voltage (Fig. 6). A function generator was used to modulate the light from a broadband LED light source (diameter = 3 cm). Sinusoidal intensity pattern was generated and transmitted through the LED. At the receiver side, peak-to-peak voltage of photodetector output was recorded (not the direct current value). This scheme allows minimization of the ambient light effect and external sources. The amplitude of output voltage changes according to the amount of coupling inside the POF core. The light source was placed in parallel and at a distance of ∼3 cm from the POF surface. The diameter of the light source was

![Fig. 5](image-url) Coating schemes (a) unpatterned POFs (3, 5, 7, and 100 mm). (b) Spiral-patterned widths of ZnO nanorod-coated POFs (3, 5, and 7 mm).
oriented along the longitudinal axis of the POF. The fiber tip was covered to avoid light entering from the end. The analysis was performed on the spiral-patterned POFs with three different widths of ZnO coatings (3, 5, and 7 mm), the unpatterned POFs with the limited ZnO coating (3, 5, and 7 mm), and full coated POF’s. Five readings were acquired for each measurement.

3.3 Multiple Optical Channel Sensing of Alcohols

Figure 7 shows the experimental setup used for optical sensing of alcohols. The apparatus consisted of a spectrometer (USB4000, Ocean Optics) and a sensing chamber (0.18 m × 0.2 m × 0.27 m). A visible white light source with wavelength 380 to 750 nm was used to induce light-side coupling. The intensity of the white light source was modulated with a periodical pattern using the modulator to minimize the background effect as illustrated in Fig. 7. It is worth mentioning that here a spectrometer was connected to the end of the POF to record the spectrum of the coupled light. During the investigation of the sensor performance, ambient air was allowed through the sensing chamber at room temperature (~26°C) and relative humidity of 45% until a steady-state condition (0 ppm) was obtained. The white light source was placed 3 cm from the POF surface. A known amount of alcohol was vaporized and introduced into the sensing chamber as the target gas. Three kinds of alcohol were tested: (1) ethanol [CH₃CH₂OH] (Merck KGaA, Germany, 99.8%), (2) methanol [CH₃OH] (J. T. Baker, 99.8%), and (3) isopropanol [C₃H₇OH] (Merck KGaA, Germany, 99.5%). The spectral response toward alcohol vapor was recorded every 10 s from 0 to 300 ppm. In the experiment, the concentration (C) of target alcohol vapor in ppm was computed using the following equation:29

\[ C = \frac{T \times V_t \times D_t}{V_c \times M_t} \times R, \]  

(4)

Fig. 6 Optimization setup to measure the output voltage for unpatterned and spiral-patterned ZnO nanorods. The tip of the POF was covered by black tape in all measurements and a modulated visible-light source was placed at a distance of 3 cm from POF.

Fig. 7 Experimental setup to validate the alcohol sensing activities of spiral-patterned POF in visible wavelength as multiple optical channels (blue, green, and red).
where $T$ is the operating temperature in Kelvin (K) and $V_c$ is the volume (ml) of the diluted target gas, which is equal to the volume of the sensing chamber. $V_t$, $D_t$, and $M_t$ represent the volume ($\mu$l), density ($g/ml$), and molecular weight ($g/mol$) of the alcohol analyte, respectively. $R$ is the universal gas constant, which is equal to $8.2 \times 10^4$. From the recorded visible spectrum (380 to 750 nm), the response from three specific ranges (referred to here as channels) was studied—blue (450 to 495 nm), green (495 to 570 nm), and red (620 to 750 nm). In the channels, the measured transmittance average values and standard deviations were obtained for all concentrations of the alcohol vapors. The sensing performances in each channel were investigated by analyzing the effects on light intensity toward all the alcohol vapor concentrations. The sensing effects were presented in term of relative intensity modulation (RIM) in an arbitrary unit (a.u.)$^{30}$ that was calculated using the following equation:

$$RIM = \frac{I_f(\text{av}) - I_i(\text{av})}{I_i(\text{av})},$$

where $I_f$ is the smallest average intensity after injection of alcohol vapor and $I_i$ is the average initial intensity before injection of alcohol vapor under light illumination. The RIMs were obtained for each alcohol vapor response in all three channels. To create an inexpensive multi-channel sensing system using red, green, blue LEDs, and a simple photodetector, a preliminary reference is developed through division of higher responses from two of the three channels with respect to the channel that produces lowest response. It is worth noting here that the aim of this part of the experiment is to study the efficiency of utilizing only three color channels (red, green, and blue) for different vapors sensing. This can possibly be extended to the use of RGB LED with lower cost photodetector instead of a spectrometer.

### 4 Results and Discussion

Figure 8 illustrates the modeling results of normalized output for unpatterned and spiral-patterned POF. The normalized output increased greatly for spiral patterned POFs over that derived from unpatterned coatings as the width of ZnO nanorods coating was varied from 0 to 20 mm. Spiral-patterned POFs coupled more light compared to unpatterned POF for nanorod coating widths <5 mm as shown in Table 1. The greatest difference in output between patterned and unpatterned coatings was shown at ZnO width equal to 1 mm where $\Delta I(1\text{ mm}) = I_p - I_{up} = 0.369$ due to spiral ZnO coating along the core POF compared to unpatterned coating that had only one patch of ZnO region (1 mm) on the POF. Although $\Delta I(1\text{ mm})$ was the highest, the coupling output for spiral pattern was not considered because it was not the maximum value of light-side coupling. The spiral pattern coating achieved the maximum value of light-side coupling at width equal to 5 mm [$\Delta I(5\text{ mm}) = I_p - I_{up} = 0.135$]. Therefore, despite that $\Delta I(5\text{ mm})$ was <$\Delta I(1\text{ mm})$, the use of maximal light-side coupling was more dominant in applications.

![Fig. 8 The output voltage for unpatterned and spiral-patterned coating by varying the width of ZnO nanorods coating on POFs.](image-url)
Meanwhile, the unpatterned coating achieved the maximum value of light-side coupling at ZnO coating width longer than spiral patterns. Once the maximum output was reached, the output remained consistent in POF’s with both types of coatings at the normalized value equal to 1 even though the width of ZnO coating was varied.

Based on simulation results, 3, 5, and 7 mm coating widths were selected for experimental optimization and application. Figure 9 shows the experimental results for spiral-patterned and unpatterned POFs. Overall, it can be seen that both coating schemes correlated well with simulations. The results clearly showed that the unpatterned coatings of ZnO nanorods (3, 5, and 7 mm) coupled less light compared to spiral-patterned POFs. In addition, the full ZnO coated POFs (100 mm) produced an output voltage that was less than spiral-patterned POFs (3, 5, or 7 mm) due to less illumination coverage of the visible-light source in the distance of 3 cm from POF sample as shown in Fig. 6.

### Table 1

<table>
<thead>
<tr>
<th>Widths of ZnO coating region (mm)</th>
<th>Spiral pattern $I_p$</th>
<th>Unpatterned $I_{up}$</th>
<th>$\Delta I = I_p - I_{up}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.699</td>
<td>0.330</td>
<td>0.369</td>
</tr>
<tr>
<td>2</td>
<td>0.910</td>
<td>0.551</td>
<td>0.359</td>
</tr>
<tr>
<td>3</td>
<td>0.973</td>
<td>0.699</td>
<td>0.274</td>
</tr>
<tr>
<td>4</td>
<td>0.992</td>
<td>0.798</td>
<td>0.194</td>
</tr>
<tr>
<td>5</td>
<td>1.000</td>
<td>0.865</td>
<td>0.135</td>
</tr>
<tr>
<td>6</td>
<td>1.000</td>
<td>0.909</td>
<td>0.091</td>
</tr>
<tr>
<td>7</td>
<td>1.000</td>
<td>0.939</td>
<td>0.061</td>
</tr>
</tbody>
</table>

**Fig. 9** The experimental result of spiral-patterned and unpatterned coating for 3, 5, 7, and 100 mm.

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### 4.1 Physical Characterization

The SEM image in Fig. 10(a) with magnification set at 10.00 kX clearly shows the spiral-patterned ZnO nanorods coating on POF. In the low-magnification image given in Fig. 10(a), the width of ZnO coating is 5 mm and the uncoated spacing is 10 mm in width. In Fig. 10(b), ZnO nanorods can be seen growing perpendicular to the surface of the POF, an important geometry to enhance the light scattering mechanism for light-side coupling into the POF. Moreover, the
growth of ZnO nanorods on POF surface in Fig. 10(b) observed at magnification of 15.00 kX reveals high density (85 nanorods/3.62 x 10^{-12} m² = 23.50 x 10^6 nanorods/μm²) and uniform distribution. Figure 10(c) shows the growth of ZnO nanorods with magnification of 30.00 kX. From the SEM images, the obtained ZnO nanorods were about 3.41 ± 0.05 μm in length and 172.8 ± 20 nm in diameter as shown in Fig. 10(d).

**4.2 Multiple Optical Channels Sensing**

The improved side coupling by the spiral-patterned coating of ZnO nanorods on POF is exploited to demonstrate sensor performances in different wavelength domains of visible light called channels to sense three different alcohol vapors (methanol, ethanol, and isopropanol) as shown in Fig. 11. All sensing was accomplished with the optimized spiral ZnO coating width of 5 mm. It was found that the sensor demonstrated three different responses for methanol, ethanol, and isopropanol vapors as a function of molecular weights (methanol < ethanol < isopropanol), relative dielectric constants, and polarity. The relative dielectric constants of methanol (33),
ethanol (24), and isopropanol (20), e.g., most likely influenced selective alcohol vapor molecule adsorption onto different crystal faces of the ZnO nanorods. The amount of vapor adsorption coupled with the region of adsorption on the ZnO, therefore, played major roles in the attenuation of the coupled light signal. Additionally, the refractive indices of methanol (1.328), ethanol (1.361), and isopropanol (1.377) also affected the interaction of light by varying the refractive index of ZnO nanorods coating. Interestingly, in the presence of methanol, the intensity was seen to decrease significantly indicating lower side coupling of light into the POF core. This was due to the change in the refractive index of the ZnO coating layer caused by methanol absorption. During sensor recovery, as methanol evaporated from the layer of ZnO nanorods coating, the sensor output was observed to return closely to the initial condition in ~7 min. For ethanol and isopropanol, the sensor also demonstrated similar response patterns caused by rising adsorption onto ZnO nanorods. However, the sensor demonstrated slight response to isopropanol vapor molecules compared to ethanol. The recovery time for ethanol and isopropanol were ~5 and ~3 min, respectively. The decrease of light intensity when exposed to the alcohol vapors and the recovery toward initial value is believed to be due to chemisorption process, the interaction of hydrogen bonding between –OH groups of alcohol molecules with ZnO coating layer. Due to the small size of methanol molecules compared to ethanol and the biggest molecule size, isopropanol, the chemisorption process between methanol molecules and ZnO coating layer is very high, taking more time to recover relatively to initial value.

The change in the refractive index of the ZnO coating layer due to absorption process that affects the amount of light scattering into POF can be explained clearly using the sensing mechanism depicted in Fig. 12. Initially, ZnO nanorods are exposed to air at room temperature as shown in Fig. 12(a). In this case, ionized oxygen is chemisorbed onto the surface in its molecular form \( \text{O}_2^- \) as given by

\[
\text{O}_2 (\text{gas}) + e^- \leftrightarrow \text{O}_2^-.
\]

As the surface is illuminated continuously by visible light as shown in Fig. 12(b), changes in the carrier density in the ZnO nanorods and the layer of depletion depth occur. Once electron–hole pairs are generated by the visible light, holes migrate to the surface and discharge the adsorbed

\[ (a) \quad (b) \quad (c) \]

\textbf{Fig. 11} Spectroscopy responses of multiple optical channels sensor in channel blue, green, and red wavelengths for (a) methanol, (b) ethanol, and (c) isopropanol.
oxygen molecules. This causes the depth of the depletion layer to decrease, resulting in the desorption of surface oxygen. Over time, unpaired electrons accumulate until the desorption and adsorption of oxygen reaches an equilibrium state. The amount of adsorbed oxygen decreases compared to air conditions as shown in Fig. 12(a). The presence of excitons under visible-light irradiation leads to the formation of atomic adsorbed oxygen, $O^-$, which is substantially more chemically active than $O_2^-$ and creates favorable conditions for catalytic reactions. This phenomena contributed to the amount of light scattering into optical core fiber by the ZnO nanorods.

When gases (such as methanol in this case) are introduced, the adsorbed oxygen on ZnO nanorods took part in the oxidation of methanol in two possible ways [Eqs. (7) and (8)].

$$\text{CH}_3\text{OH} + O^- \leftrightarrow \text{HCHO} + \text{H}_2\text{O} + e^-,$$  \hspace{1cm} (7)

$$\text{CH}_3\text{OH} + O_2^- \leftrightarrow \text{HCOOH} + \text{H}_2\text{O} + e^-.$$ \hspace{1cm} (8)

As a result, scattering attenuation was therefore a function of the type of molecular species adsorbed onto the ZnO surface (e.g., its refractive index, $n$) and the amount of that material present, allowing these molecules to interact differently with the incoming light. At the same time different organic molecules have different refractive indices, molecule sizes, and band bending occurs at surface, which will also affect the interaction of incoming light by varying the $n$ of the outer coating differently.

As observed from the responses of the sensor in multiple optical channels as shown in Fig. 13, different wavelengths of light contributed in determining the amount of chemical vapor absorption onto ZnO nanorods with attenuated light scattering into the POF core. In this result, the green channel presented the largest range of intensity (0.11 to 0.87) followed by the blue channel (0.07 to 0.41) and then, with the lowest intensity, the red channel (0.05 to 0.17). It can be concluded that the intensity of green light in ZnO nanorods dramatically decreased with the increase in vapor concentration as alcohol molecules are adsorbed onto the ZnO coating. Subsequently, there was a degree of attenuation of light scattering into POF core. It was shown in Refs. 39–41 that the luminance characteristic of ZnO has a significant response in green spectral range due to the strong influence by free-carrier depletion at the particle surface, particularly for small ZnO particles.
Moreover, upon exposure to visible light, ZnO nanorod coating will be photoactivated leading to reduced intergrain barrier height, thereby increasing the density of free carriers in the material. Boiling points of primary alcohols in these experiments are methanol: 65°C; ethanol: 78°C; isopropanol: 82°C, which are related anyway to the bond dissociation energies. Hence, the order of RIM was in the reverse order. This leads to the specific heats of vaporization, which is the lowest for isopropanol (0.471 kJ/g) compared to ethanol (0.925 kJ/g) and methanol (1.22 kJ/g). At concentration <100 ppm, the sensor demonstrated a slight difference in response to methanol and ethanol vapor. It means that the sensor is not able to differentiate significantly the two alcohol vapors due to less amount of vaporization to extremely excite oxygen ions on the surface of ZnO coating. A significant difference can be seen clearly when the sensor was exposed to higher concentrations because the interaction between methanol molecules and the oxygen ions of ZnO contributed to a higher carrier concentration compared to ethanol.

**Fig. 13** The responses of multiple optical channels sensor as a function of concentration of methanol, ethanol, and isopropanol vapors (ppm) in channels (a) blue, (b) green, and (c) red.
Figure 14 shows the RIMs of the multichannel optical sensor for alcohol vapors. The RIMs of the sensor in each channel were calculated using Eq. (5). The absolute value of the light intensity decreased rapidly with increasing alcohol vapors concentration from 0 to 300 ppm. The green channel contributed the highest RIM for all three alcohols. Measurements in the blue light domain showed intermediate RIM, and lastly, the red channel exhibited significantly lower RIM of all three light domains for all alcohols tested. For the green channel, the sensor response for methanol was found to be 0.84 a.u. However, when ethanol and isopropanol were tested, the RIM decreased to 0.55 and 0.14 a.u., respectively. In the case of the blue channel, sensor
response to methanol also presented the highest RIM of the three alcohols equal to 0.79 a.u. For ethanol and isopropanol, once again, decreased but to lower levels than those observed for the green channel 0.49 and 0.13 a.u., respectively. The same trends in alcohol RIM based on molecular weight was demonstrated by the red channel but to the lowest levels of the three light domains. The optimum RIM for isopropanol is smaller than that of ethanol due to reduced absorption onto the ZnO nanorods by the larger molecular weight and slightly less polar molecule. Channel green demonstrated significant RIM in sensing the three alcohol vapors because ZnO nanorods have both polar and nonpolar surfaces as reported in Ref. 42, where zinc vacancies (VZn) at the nonpolar surfaces are responsible for the green luminescence of ZnO nanostructures. The presence of neutral VZn on ZnO coating generates a multiple effect: the absence of Zn ions leaves out under coordinated O atoms, and the unpaired O electrons give rise to empty states. As a consequence, this leads to a high absorption in green luminescence due to strong O–H chemical bonds.

A preliminary reference was developed by performing cross validation on channel blue and green with respect to channel red that produced the minimal response for the alcohol vapors as shown in Fig. 15 to create an inexpensive multichannel sensing system using red, green, blue LEDs, and a simple photodetector. To observe the response of the sensor as a multichannel device, one of the three channels is set as a reference to accommodate for source fluctuation and environment effect (e.g., heat and vibration). The other two readings are normalized to the reference and the RIM of different gas vapors to these channels are examined. In both validations, the three alcohol vapors illustrated a similar pattern response at two different ranges, which were ~1.3 to 2.5 for channel blue/channel red and ~2.0 to 5.2 for channel green/channel red. In these ranges, significant responses were seen clearly in methanol and ethanol sensing compared to isopropanol that showed less response.

5 Conclusion

The present study optimized theoretically the width of the ZnO nanorod spiral coating and demonstrated experimentally with a visible-light source its utility as an alcohol vapor sensor. The width was found to be 5 mm for efficient light-side coupling. There was reasonable correlation between theory and experiment. Practical application of the special POF system showed promise as a multiple optical channel sensor for alcohol vapors in the visible range of the spectrum. To explain the mechanism of sensing for alcohols, we proposed that the light scattering aspect of the ZnO nanorods dependent on changes in the refractive index was affected by adsorption of alcohol species. With regard to sensing performance in the three spectral channels described previously, methanol showed the greatest RIM and range followed by ethanol and isopropanol. In the investigation of a multiple optical channel sensor, the green channel significantly produced higher RIMs in sensing methanol, ethanol, and isopropanol vapors compared to the blue and red channels. Furthermore, a preliminary reference was developed to propose a multiple optical channels sensor system using inexpensive color LEDs (blue, green, and red) as light sources and a simple photodetector in applications.

Acknowledgments

The authors would like to acknowledge the University of Malaya for their financial support under a High Impact Research Grant under Grant No. D000009-16001.

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Biographies for the authors are not available.