Light backscattering (e.g. reflectance) by ZnO nanorods on tips of plastic optical fibres with application for humidity and alcohol vapour sensing

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Relative humidity and alcohol vapour sensing by light backscattering was demonstrated by zinc oxide (ZnO) nanorods grown on tips of plastic optical fibres. Synthesis of ZnO nanostructures was accomplished by the hydrothermal method. A new technique was proposed to extract the backscattered light by ZnO nanostructures. The system was shown experimentally to sense moisture and alcohol vapours. Three ranges of the visible spectrum blue (450–500 nm), green (500–570 nm) and red (610–700 nm) were studied in experiments. Spectral reflectance based on backscattering from ZnO surface structures was used to measure the amount of light backscattered by ZnO nanorods. Results showed that light in the red visible range of the spectrum had higher sensitivity and reflectivity compared with blue and green spectral ranges.

1. Introduction: Zinc Oxide (ZnO) has attracted intense research interest due to its widespread application especially for biological sensing and gas sensing [1–3] and optoelectronics [4], energy storage [5] and solar cells [6]. ZnO is a typical group II and IV semiconductor material with a wide bandgap of 3.37 eV at room temperature and high-excitation binding energy of 60 meV, suitable for short wavelength optoelectronics applications. ZnO can be synthesised using gas phase deposition or chemical phase techniques such as the hydrothermal method [7]. Hydrothermal techniques require low temperature (<100 °C) with straightforward control of nanorod morphology by variation of experimental conditions. The hydrothermal method therefore provides an effective, easy and simple route for nanorod synthesis. Synthesis on flat and cylindrical surfaces has been extensively demonstrated [8–10]; however, synthesis on tips of optical fibres still remains relatively challenging. For example, ZnO synthesis on flat surfaces such as glass substrates results in highly oriented and order arrays [8, 9]. On the other hand, cylindrical surfaces, especially those encountered on optical fibres, require pre-surface treatment to ensure high-order and strong attachments [11].

Typically, light backscattering involves light reflected at different angles from the surface facets of the medium (diffused reflection due to scattering) back to the direction of the source. Light backscattering is used in fibre applications to characterise loss, irregularities and imperfections in the optical fibre [12]. Loss and irregularities are measured by launching light into the optical fibre core. Light propagation in the optical fibre is then scattered in many directions once the light contacts a defect or irregular surface. Only a small portion of the scattered light is backscattered [13]. The backscattered light is then measured as a function corresponding to the position corresponding to the position along the fibre in order to locate the sources of loss and irregularities in the optical fibre [14].

On the basis of limited study on the backscattering of light by ZnO nanorods, it was found that the amount of backscattered light depends on the diameter, length and density distribution of the ZnO nanorods [15]. The increase of ZnO nanorod diameter, length and distribution all serve to increase the random multiple scattering of light. In addition, higher-order multiple scattering modes also enhance backscattering. It is this source of backscattered light that can be exploited for humidity and alcohol vapour sensing. In this case, due to adsorption of water of alcohol molecules, the refractive index of the ZnO is changed. This results in reduction of forward scattered light and a concomitant increase of backscattered light. Nanorods create random multiple scattering facets causing free path propagation with neighbouring nanorods (Fig. 1). When ZnO is exposed to water vapour, rapid surface adsorption of water molecules occurs and creates water molecules layer onto the ZnO nanorods. These interactions between water molecules and ZnO nanorods change the effective refractive index leading to backscattering by ZnO nanorods.

In this work, we report the successful synthesis of ZnO nanorod growth on tips of plastic optical fibre (POF) surfaces via the hydrothermal growth method and the demonstration of enhanced light backscattering by the ZnO nanorods in three visible spectrum domains. Finally, we apply the backscattered concept for humidity and alcohol sensing.

2. Experiment details: Standard multimode CK-80 POFs (Mitsubishi Rayon Co. Ltd.) of length 20 cm with core and cladding 1960 and 2000 µm, respectively, were used in experiments. About 5 cm from the tip of the POF was covered with electrical tape to ensure the ZnO only growth on the tip. POFs were then dipped into the mixture of 'Tween 80' [$C_{64}H_{124}O_{26}$, Sigma-Aldrich] surfactant and de-ionised (DI) water for pre-treatment. Fig. 2 shows the POF pre-treatment process.

2.1. ZnO seeding procedure: The ZnO seed solution was made by adding 0.0044 g of zinc acetate dihydrate [Zn $(O_2CCH_3)_2{\cdot}2H_2O$, Merck] into 60 ml of pure ethanol to form 1 mM solution under stirring at 60 °C. Then following cooling, 20 ml of pure ethanol was added. After addition of the ethanol, 0.0008 g of sodium hydroxide [NaOH, Merck] in 20 ml of ethanol was added to make 1 mM solution. The seed solution was kept in a water bath at 60 °C for 3 h. To provide nucleation sites for ZnO nanorod growth, the POFs were placed on a hot plate at 60 °C. The seeding solution was applied drop-wise onto the tips of the POFs.

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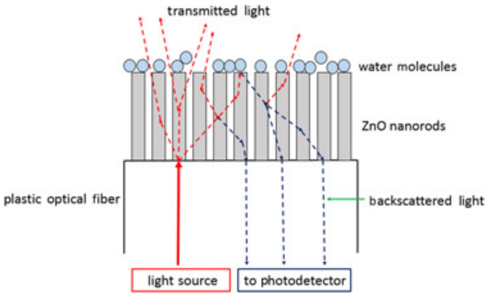

Fig. 1 *Light backscattering by ZnO nanorods with the presence of water molecule for humidity sensing applications*

The dropping process was repeated ten times. Following the conclusion of the dropping process, the POFs were annealed at 60 °C for 3 h.

2.2. ZnO nanorod synthesis: ZnO nanorods were grown on seeded POFs by application of the hydrothermal process. A 10 mM aqueous solution of 2.9747 g zinc nitrate hexahydrate [$Zn(NO_3)_2{\cdot}6H_2O$, Ajax Finechem Pty Ltd.] and 1.4019 g hexamethylenetetramine [$(CH_2)_6N_4$, Sigma-Aldrich] were added to 1000 ml of DI water. POFs were vertically dipped (5 cm deep from the tip of the POF) into 300 ml of the synthesis solution and placed in an oven at 90 °C. Growth times were varied as follows: 8, 10, 12 and 15 h. Growth time were varied to study the impact of ZnO nanorod size and density on the magnitude of light backscattering. The solution was changed every 5 h in order to maintain a constant growth rate.

2.3. Characterisation of ZnO: Scanning electron microscopy (SEM) was accomplished to image ZnO nanorods with a Hitachi S-3400N series SEM.

2.4. Optical theory and measurements: Fig. 3 illustrates the light propagation and backscattering mechanism of the sensor probe. Incident light with intensity were under the beam splitter and transmitted to the POF surface (I_i T_{BS}). Owing to the irregularities of the POF surface, some part of light that transmitted are reflected to the beam splitter (I_i R T_{BS}) and to spectrometer, and other parts of light are transmitted into the POF [I_i T_{BS} $(1–R)$]. Then, light that are transmitted into the POF are backscattered by the ZnO nanorods with magnitude equal to $I_i(1-R)T_{BS}R_{ZnO}$ where T_{BS} represents the transmittance of light by the beam splitter. I_i is the intensity of light from the source. R is the reflection from air to the POF surface and $(1-R)$ are the transmissions from air to POF surface. R_{ZnO} is an amount of light backscattered by the ZnO nanorods in terms of sum total

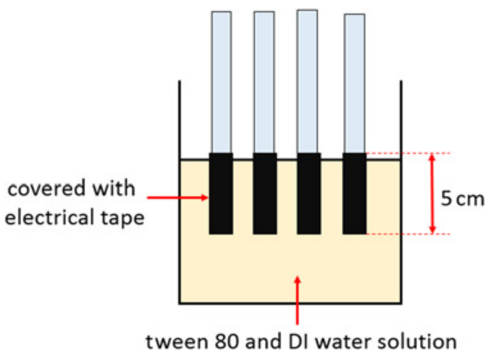

Fig. 2 *POF pre-treatment process by dipping the POF covered with electrical tape into the mixture of Tween 80 and DI water solution*

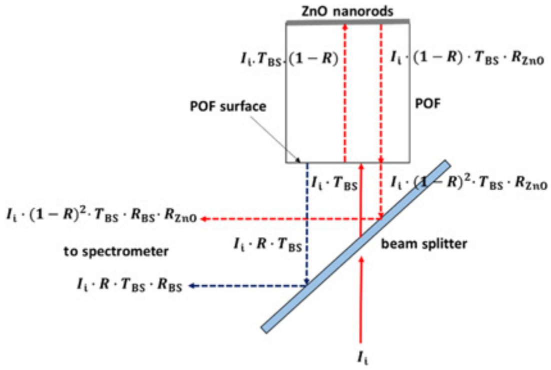

Fig. 3 *Light propagation and backscattering measurements in the sensor probe. I_i is the intensity of light from the source, R_{BS} and T_{BS} denote as light reflection and transmission of light by the beam splitter, R represents the reflection of POF and air and R_{ZnO} is the amount of light backscattered by ZnO nanorods*

reflectivity. Backscattered light then transits to the POF surface and is directed to the spectrometer by the beam splitter with magnitude equal to $I_i(1-R)^2R_{BS}T_{BS}R_{ZnO}$. Equation (1) expresses the intensity of backscattered light by ZnO nanorods and (2) expresses the light reflected from bare POF tip surfaces without ZnO nanorods

$$I_{ZnO} = I_i R\, T_{BS} R_{BS} + I_i\,(1-R)^2\, T_{BS}\, R_{BS}\, R_{ZnO} \tag{1}$$

$$I_{bare} = I_i\, R\, T_{BS}\, R_{BS} + I_i\,(1-R)^2 T_{BS} R_{BS} R \tag{2}$$

Dividing (1) by (2)

$$\frac{I_{ZnO}}{I_{bare}} = \frac{(1-R)^2(R_{ZnO}/R)+1}{(1-R)^2+1} \tag{3}$$

where R is the reflection for POF given by

$$R = \left|\frac{n_1 - n_2}{n_1 + n_2}\right|^2 = \left|\frac{1.5-1}{1.5+1}\right|^2 = 0.04 \tag{4}$$

n_1 and n_2 are the refractive indexes of POF and air

$$(1-R)^2 = (1-0.04)^2 \simeq 1 \tag{5}$$

Substitute (5) into (3)

$$\frac{I_{ZnO}}{I_{bare}} = \frac{(R_{ZnO}/R)+1}{2} \tag{6}$$

Thus, the amount of backscattered light in terms of reflectivity can be expressed by the following equation:

$$R_{ZnO} = R(2\sigma - 1) \tag{7}$$

where σ is the ratio of intensities light backscattered by ZnO and the bare surface without ZnO (8)

$$\sigma = \frac{I_{ZnO}}{I_{bare}} \tag{8}$$

2.5. Experimental results: Fig. 4 shows the experimental scheme of the sensor. The setup consisted of a humidity chamber (17 cm × 17 cm × 12 cm), a spectrometer (compact charged coupled device (CCD), Thorlabs), an indoor–outdoor hygrometer–thermometer and

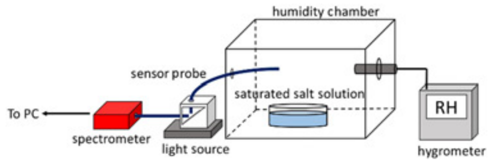

Fig. 4 *Schematic diagram for the proposed humidity sensor. The hygrometer can measure both humidity and temperature*

a sensor probe mounted to an ultra-white light-emitting diode (LED) light source. A small dish filled with salt was placed under the sensor probe and hygrometer, to produce moisture inside the chamber. The salt solution contained 3.1614 g NaOH [NaOH, Merck] dissolved in 60 ml of DI water. During experiments, the temperature inside the chamber was held at a constant 26 °C – consistent with the temperature outside of the chamber. The spectrometer was placed outside the chamber opposite to the hygrometer. The POF of the sensor probe was attached to an ultra-white LED light source and equipped with a 9 V power source. An indoor–outdoor hygrometer–thermometer was used to measure the relative humidity (RH) inside the chamber and temperature inside the chamber and surroundings, respectively. Spectral acquisition was accomplished every 10 s.

Fig. 5 shows the schematic diagram of the alcohol vapour sensor. For alcohol vapour sensing, three different alcohols – methanol, ethanol and 2-propanol – were tested. The sensing chamber (25 cm × 17 cm × 17 cm) was equipped with inlet and outlet tubes, and rubber tubes to transport the vapour from cylinder flask into the chamber. Alcohol was first heated using a hot plate until boiling was observed. Alcohol vapour produced from the flask was then passed into the test chamber through the rubber tubing until a steady-state condition (until the vapour constantly produced inside the chamber) was obtained. The chamber was vented to the atmosphere surrounding the chamber. The same sensor probe used for humidity sensing was used in the experiment to test the stability of sensor, the probe used from humidity sensing was left dried for a few hours and then same probe was tested to alcohol vapour sensing. Three spectral channels were applied in experiments to test sensitivity to light backscattering: blue (450–500 nm), green (500–570 nm) and red (610–700 nm).

3. Results and discussion: Figs. 6*a* and *b* show the SEM images from side and top views, respectively, showing high-density distribution of ZnO nanorods. Fig. 5*c* depicts the SEM low-magnification view on tip of POF surface. The diameter and length of nanorods are estimated for 12 h growth time to be around 250 and 1000 nm, respectively.

3.1. Reflectivity measurement: Fig. 7 shows the reflectivity [deduced from the measured intensities using (7)] at different growth times with respect to red, green and blue spectrum. The highest reflectivity can be achieved at 12 h growth time. At 12 h growth time provide increment in length diameter and density

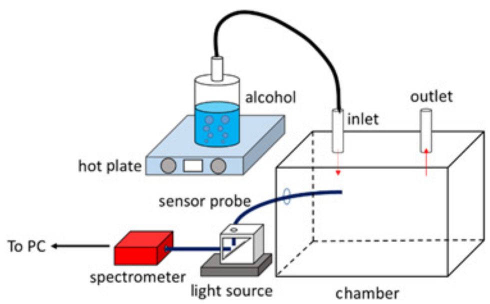

Fig. 5 *Schematic diagram depicting the alcohol vapour sensor setup*

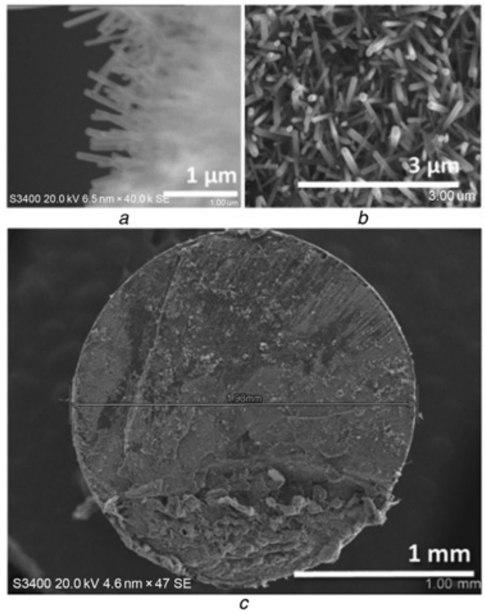

Fig. 6 *SEM images from side and top views showing high-density distribution of ZnO nanorods*
a High magnification views of ZnO nanorods from the top and side views
b, c SEM low-magnification view of the tip of POF surface coated with ZnO nanorods

distribution compared with 8 and 10 h. Bora *et al.* [16] has reported the effect of growth time variation on length and diameter of ZnO nanorods. In his report, increasing the growth time can increase the length and diameter of nanorods. However, in 15 h growth time, light is significantly dropped since the increment of diameter and length has limited the density of nanorods on tip of POF, thus reduced the multiple scattering by ZnO nanorods.

3.2. Sensor measurement: Fig. 8 shows the reflectivity at three different visible spectral ranges with respect to RH. Fig. 8 depicts that reflectivity increases as the RH increases and later constant at 93% RH. The ZnO nanorods are exposed to an environment of humidity which causes rapid surface adsorption of water molecules forming a water molecule layer onto the nanorods. The surface adsorption layer will modulate the optical properties of ZnO by means can change the effective refractive index and absorption coefficient of ZnO nanorods surfaces. The increases in RH will lead to increase in the water molecules adsorbed by the nanorods. As the light hit the nanorods that adsorbed the water molecules, more light will randomly backscatter. Also in Fig. 8,

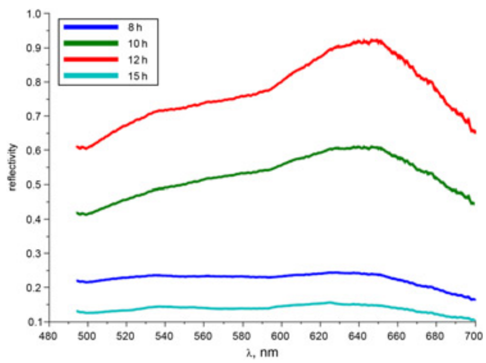

Fig. 7 *Reflectivity in visible spectrum at growth durations 8, 10, 12 and 15 h*

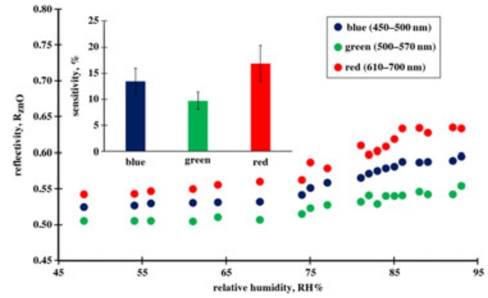

Fig. 8 *Reflectivity at three different visible spectra. Inset shows the sensitivity of the proposed sensor at different visible spectra with respect to RH*

the reflectivities are slightly changed at humidity at below 60%. This caused by surface adsorption only takes place on the surface of the nanorods at medium humidity (40–70%RH). While in higher humidity (70% onwards) condensation occurs and creates a meniscus film onto the nanorods that change the refractive index allowing more light backscattered [17]. The sensitivity of the proposed humidity sensor was shown in the inset of Fig. 8. As seen in the inset, red spectrum provides higher sensitivity (16.81%) followed by blue (13.40%) and green (9.68%). Green spectral has the lowest sensitivity because of ZnO luminescence property in green spectrum [17] shows that absorption of light by ZnO occurs higher in range green spectrum and lower at red spectral ranges.

In other experiment, Fig. 9 shows the reflectivity for red spectrum at different concentration of alcohol. The results indicated that methanol is able to provide higher backscattering compared with ethanol and 2-propanol due to the size of alcohol molecules interact with ZnO nanorods which can modify the effective refractive index of nanorods. The sensor output was observed returning to its initial condition as the alcohol evaporated from the ZnO nanorods surfaces. Inset in Fig. 9 illustrates the sensitivity of ethanol, methanol and 2-propanol at different visible spectrum. In methanol, sensitivity for the red spectrum is 27.2% and sensitivity was reduced to 10.53 and 7.85% for ethanol and 2-propanol. For the green spectrum, methanol possessed highest sensitivity about 12.14%. The sensitivity was decreased to 4.61 and 4.73% for ethanol and 2-propanol. The blue spectrum exhibits the same graph trends as red spectrum.

In initial condition, ZnO is exposed to the air, an oxygen molecule (O_2) adsorbs on the surface of nanorods and O^- ion was formed by capturing an electron from the conduction band, forming a depletion layer which controls the density and mobility of electron in the nanorods [18]. When ZnO nanorods are exposed to the alcohol vapour environment, the alcohol molecule will react with O^- ion and release electron which will migrate to conduction band of the nanorods, resulting in the reduction of the amount of surface adsorbed of oxygen ions. As the concentration

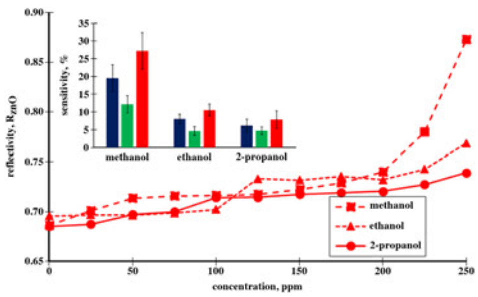

Fig. 9 *Reflectivity at three different alcohols with respect to concentration in red spectrum. Inset shows the sensitivity of the sensor at different visible spectra and alcohol vapour*

of alcohol vapour inside the chamber increase, the amount of surface adsorbed is reduced, thus alcohol molecules interaction with nanorods is increased. When the nanorods are exposed back to the air environment, the adsorbed alcohol leaves the surface of nanorods and O^- is adsorbed back (desorbed) to the surface of nanorods. In addition, size of alcohol molecules are most likely influencing the surface adsorption of alcohol molecules onto ZnO nanorods. Yim *et al.* reported that methanol has the smallest molecular sizes compared with ethanol and 2-propanol [19]. When the nanorods are exposed to alcohol environment, the smaller-sized alcohol molecules, for example, methanol will interact more with nanorods compared with bigger-sized molecules which can affect the scattering of light by nanorods. Interaction of alcohol molecule of surface adsorption of alcohol molecules onto nanorods can cause change in effective refractive index resulting more light will be backscattered and the refractive index keeps increasing as the concentration of alcohol increase.

4. Conclusion: In summary, the present Letter proposed a light backscattering by ZnO nanorods growth on the tip of POF surfaces with their potential application as simple and cost-effective optical sensor to sense humidity and alcohol vapour. The ZnO nanorods were grown using hydrothermal techniques and undergo the pre-treatment to achieve strong attachment of ZnO nanorods on the POF. This work also presented a new technique to collect the backscattering of light by ZnO nanorods at different visible spectra. Then, the techniques were experimentally demonstrated showing the variation of reflectivity in the presence of water and different alcohol vapours at different visible spectrum. Rapid surface adsorption of water and alcohol vapours onto ZnO nanorods surfaces modulates the refractive index and optical absorption of ZnO nanorods. ZnO luminescence property regulates the light absorption of ZnO nanorods. Red spectrum shows a higher sensitivity compared with blue and green.

The proposed light backscattering sensors have limitation in sensing humidity below 60% RH and alcohol concentration below 200 ppm. Several new aspects need to be considered for further improvement. For example, the doping ZnO with other materials such as aluminium, boron, indium or other group-III metals. Doped-ZnO is expected to improve the electrical and optical properties, thus enhanced the light backscattering. The reflectivity is expected to be increased with the increase of sensitivity.

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