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Graphene Oxide Functionalized Optical Planar Waveguide for Water Content Measurement in Alcohol

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Abstract: An abrupt change in optical transmission characteristic of a graphene oxide (GO) coated optical planar waveguide was observed. This observation was based on the peculiar characteristics of the graphene oxide film, namely its high transverse-electric polarized light propagation loss, highly selective permeability of water, and change in optical propagation characteristic in the presence of water. The as-fabricated GO-coated optical waveguide showed a large polarization dependent loss of ~32 dB in the C-band optical fiber communication window (1550 nm). The response of the proposed sensor was first tested by using water. When a drop of water was applied onto the GO coating, the large polarization dependent loss was fully suppressed almost instantaneously. This effect was reversible as the polarization dependent loss was restored after complete water evaporation from the GO coating. All-optical measurement of water content in alcohol was then demonstrated by using the GO-coated optical waveguide. By analyzing the drying profile of the water-alcohol mixture, water content in the range of 0.2 volume% – 100 volume% could be measured. These measurements were carried out by using solution volume of 1.0 μL only. The all-optical sensing nature of the proposed sensor has potential applications in in-situ monitoring of water content in alcohol.

Keywords: Graphene oxide; water content; alcohol solution; optical waveguide

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1. Introduction

Alcohol solutions are widely used in both laboratory and industrial applications such as chromatography analysis, food and beverage and pharmaceutical processing, and biofuel. In most of the applications mentioned above, control of water content in the alcohol solutions is critical, as it can affect the process rate and efficiency, as well as the polarity of phase in chromatography. Therefore, determination of water content in aqueous solutions of alcohol is essential. The standard method of determining water content in alcohol solutions is Karl-Fischer titration [1], which produces highly accurate and reliable results. However, skilled personnel are required to carry out the measurements, and the sample preparation processes are complex and involve the use of toxic chemicals. Alternative methods developed over the past few years employed gas chromatography, optical

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colorimetric sensing, mass spectroscopy, and ultrasonic sensing techniques, which reduce the complexity of the measurement process [2–7]. However, most of these methods require the specialized equipment and controlled environment to carry out the measurements, which limits the viability of in-situ measurement.

In the past few years, graphene oxide (GO) has attracted much attention in photonics applications due to its unique optical properties [8–10]. In 2007, Dikin *et al*. successfully fabricated a free-standing paper-like GO film, commonly known as GO paper [11]. Later, Nair *et al*. reported the peculiar filtration characteristic of GO paper with strong filtration of even the smallest gas atoms/molecules such as helium and hydrogen but exceptionally high permeation of water vapor [12]. The water transport in GO paper was modelled by Danil *et al*. [13] and Wei *et al*. [14], who explained that the separation between the GO layers in GO paper is highly dependent on the water content in the film. Without the presence of water, separation between GO layers is only about 0.4 nm which prevents liquids as well as gases to pass through. However, in the presence of water, this spacing will expand to more than 1 nm which can then allow ice-like mono or bi-layer water molecules to slide in between 2 neighboring GO layers due to the weak ice-graphene Van der Walls interaction. It was also found that GO paper exhibits strong anisotropic complex dielectric function upon interaction with light [15]. As a result, a GO-coated waveguide polarizer which induces high loss for TE-mode propagation while maintaining high TM-mode transmission was demonstrated [10].

In this work, we demonstrated that the presence of water in the GO coating would alter its optical properties, resulting in the suppression of the polarization selective capability of a GO-coated optical waveguide. We then studied the measurement capability of water content in the water-alcohol mixture solution by using the GO-coated optical waveguide. Water content in the water-alcohol solution was obtained by measuring the drying profile of the solution mixture after it was applied on the GO-coated optical waveguide. The device showed a distinguishable response to water content between 0.2 vol.% and 100 vol.% by using water-alcohol solution mixture volume of only 1 μL. Water permeation into the GO coating was almost instantaneous, while the small mixture solution volume required allowed each measurement to be completed within a relatively short period of time.

2. Experimental method

The schematic diagram of the experimental setup is shown Fig. 1(a). The polymer based waveguide was fabricated on a silicon substrate with benzocyclobutene (BCB) 4024-40 polymer coating as the under-cladding layer. BCB with a thickness of 6.1 μm and a refractive index of 1.5538 – measured at 1550 nm by using Sairon Technology SPA-4000 prism coupler – was spin-coated on the silicon substrate and cured at 250 ℃ for 1 hour. The SU-8 polymer with a refractive index of 1.569 measured at 1550 nm was then spin-coated onto the BCB under-cladding layer and patterned by using the contact photolithography technique. The SU-8 waveguide fabricated had a dimension of 5 μm in height and 10 μm in width. The sample was then subjected to a second curing process at 80 ℃ for 4 hours. After that, the cured sample was cut into waveguide chip of about 1 cm in length and bonded carefully with optical fiber interconnects by using NOA-65 UV-sensitive resin for optical signal coupling.

The GO solution was prepared by using an improved version of Hummers' method [16]. The GO solution had a concentration of 4 μg/μL by using de-ionized water as the solvent. 2 drops of 0.5 μl GO solution were then applied directly onto the polymer waveguides via the drop-casting method. Drop-casting of GO solutions to form the uniform GO film (GOF) was demonstrated by Sun *et al*. [17]

as well as in our previous work [10]. By using multiple solution drops with smaller volume instead of one large volume solution drop helps to produce a smaller coated region on the waveguide while obtaining a thick GO coating layer to reduce the footprint of the proposed sensor. The sample was then allowed to dry in the ambient condition for several hours. Figure 1(b) shows the SEM image of the orderly stacked GO coating cross-section. The average thickness of the GOF was measured by using Dektak D150 surface profiler and was 0.75 µm. The interlayer spacing of GO layers was calculated from the X-ray diffraction (XRD) spectrum, shown in Fig. 1(c), and was found to be about 0.55 nm. It is worth noting that the adhesion of the GO coating to the waveguide was very strong where it could only be removed by strong physical scratching. The polymer waveguide not coated with the GO coating was covered by using NOA-65 UV-sensitive resin to ensure that only the GO coating is exposed to the measurands in subsequent studies.

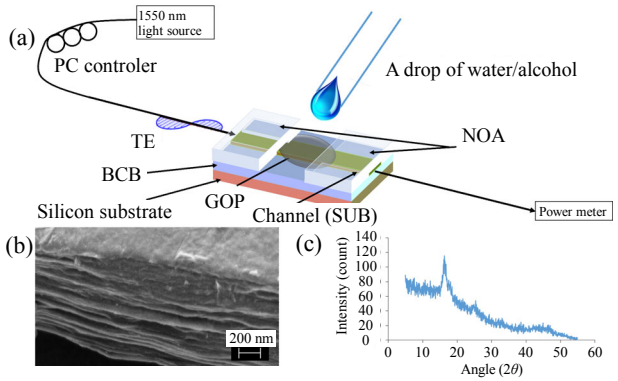


Fig. 1 Setup of the proposed graphene oxide planar waveguide water content sensor and characterization results: (a) schematic diagram of the water detection experimental setup by using the proposed GO-coated waveguide sensor; (b) scanning electron microscope (SEM) micrograph of the GO coating with orderly stacked GO layers, confirmed by (c) XRD spectrum of the GO coating with distinct peak corresponding to 0.55 nm interlayer spacing.

A 1550 nm light was coupled into the GO-coated optical waveguide via the fiber butt coupling technique. The input power of the 1550 nm light was set at –2 dBm to avoid the thermal reduction of GO during the measurement. The polarization state of the 1550 nm light was controlled by adjusting the polarization controller placed along the input fiber. The optical polarization state transmitted through the GO-coated optical waveguide was measured by using a polarimeter (Thorlabs PAX 5710). The transmission of TE-polarized light was very low – more than 30 dB lower compared with TM-polarized light transmission. The low TE-polarized light transmission was due to the significant absorption of electric field parallel to the GO layers [10]. Throughout the optical measurement, the polarization of the incident light was set to TE-polarization by using a polarization controller (PC). The position of the launch fiber was fixed to ensure that the set polarization state of the incident light was not scrambled by minor disturbance to the fiber. Also, the polarization dependent loss between TE- and TM-polarized modes of the incident light of another polymer waveguide without the GO coating was measured and found to be lower than 0.5 dB, limited by the performance of the PC. By using the information obtained above, and with the refractive index of the GOF and water-alcohol solution approximated to 1.655 and 1.33 respectively, the mode field distributions of TE-polarized light in the GO-coated waveguide with its exposed region covered with air and water-alcohol solution were simulated by using the finite element method (FEM). The optical response of the GO-coated waveguide to water was first investigated. To simulate the presence of water, 1 µL of water droplet was applied directly onto the GO coating by using a micro-pipette and the change in transmitted power of the GO-coated waveguide was recorded in 0.5 second intervals and the results were analyzed. Visual observation of the GOF was done by using a long working distance microscope (Nikon SMZ 1000). It should be noted that measurement by using such minute volume of liquid is prone to environmental effects such as variation in temperature, humidity, and air flow. Therefore, all optical measurements were carried out in a controlled environment with temperature of

(25 ± 2) ℃ and relative humidity of (55 ± 5)%RH.

3. Results and discussion

The mode profiles of TE-polarized light in the GO-coated waveguide when the GO-coated region was covered by air and water-alcohol solution are shown in Figs. 2(a) and 2(b), respectively.

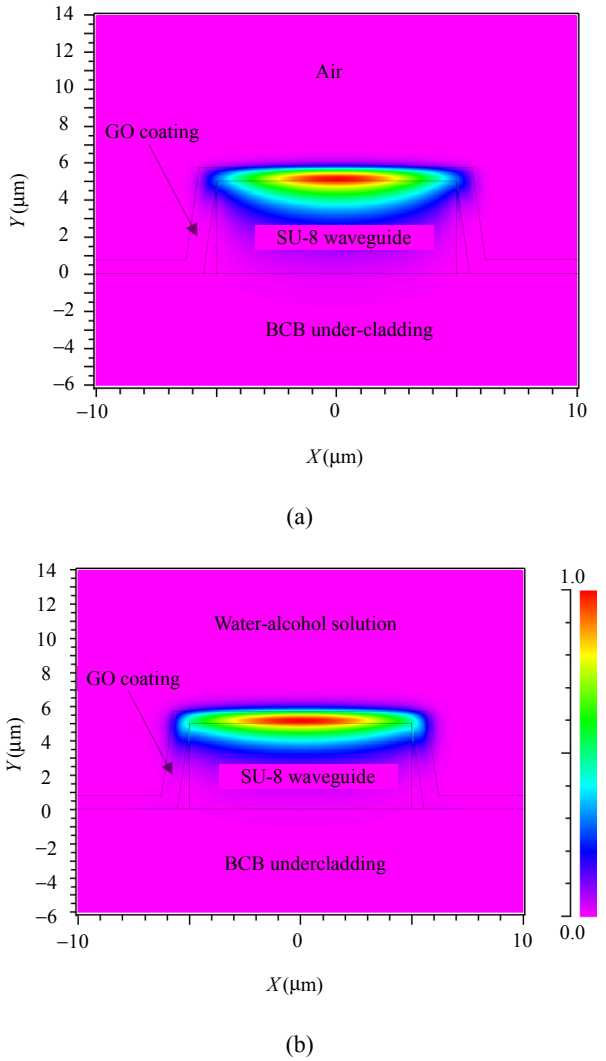


Fig. 2 Mode field distribution of TE-polarized light in the GO-coated waveguide with the GO-coated region is surrounded by (a) air and (b) water.

It can be seen that both conditions show a substantial portion of the light field distribution in the GOF. In the case where the GO-coated region is covered with water-alcohol solution, light field distribution in the GOF is slightly larger compared with the case of coverage by air. This is due to the relatively lower refractive index contrast between GOF and water-alcohol solution compared with that between the GOF and air. Nevertheless, it can be predicted that the introduction of the water-alcohol solution onto the GO-coated waveguide region will not change the distribution of the light field in the GOF significantly.

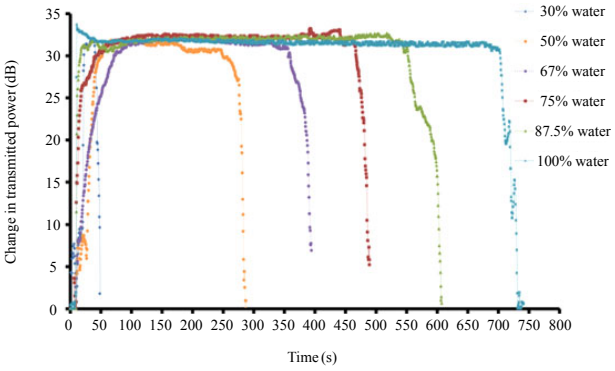
The response of the proposed sensor when a 1 μL water droplet (100%) was applied on to the GO coating is shown in Fig. 3. When water was applied, the transmitted power of the sensor increased almost instantaneously by 32 dB, approaching its TM-polarized light transmitted power level. The transmitted power remained high (for $t < 704$ s) as long as water was physically present on the GO coating. At the 704th second (~12th minute), the transmitted power reduced to its initial value (before the application of water droplet) due to the complete evaporation of water from the GO coating. The time taken for the transmitted power to decrease to its initial value was approximately 30 s, which was the time taken for the water in the GO coating to recede from the edge of the GO coating towards its center during the final phase of water evaporation, as observed by using the long working distance microscope.

An increase in transmission power when water droplet was applied was due to the change in the GO coating optical properties where it no longer absorbed the TE-polarized light power. This phenomenon was verified by observing the polarization state of the transmitted light by using the polarimeter. When the incident light was adjusted to TE-polarization by using the PC, the polarimeter measured a low optical power with the TM-polarized state. This was the residue amount of the TM-polarized light not filtered by the PC due to its performance limitation. However, when water droplet was applied onto the GO coating, the transmitted power increased and the transmitted light measured by the polarimeter showed the strong TE-polarization state. Rotating the PC would only

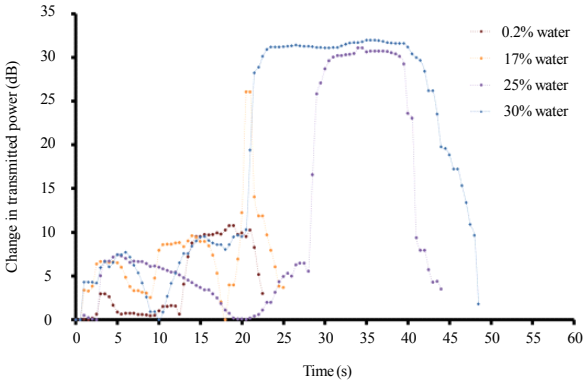
rotate the polarization state of the transmitted light with no significant variation to the transmitted power as long as water still covered the GO coating. The suppression of TE-mode absorption by the GO coating in the presence of water was still being studied. One of the reasons was believed to be the change in dielectric properties of the GO coating in the presence of water. As has been reported by Nair *et al*. [12], water readily permeated into the GO film of up to 10 μm in thickness. The permeated water molecules would readily interact with the oxygen functional groups of the individual GO layers [18, 19]. The result was the further opening of the GO layers bandgap and a corresponding decrease in conductivity [20–22]. Therefore, the propagation loss of the TE-polarized light in the GO coating was reduced, resulting in an increase in the transmission of the TE-polarized light.

The significant change in transmitted power of the proposed sensor when only 1 μL of water droplet was applied on the GOF indicates that the sensor is sensitive to even smaller volume of water. To study the sensitivity of the GO-coated optical waveguide to water content, 1 μL of water-alcohol mixture solution with different mixture ratios was applied on the GO coating and the change in transmitted power over time was measured. The alcohol used was iso-propanol (IPA). The GO-coated optical waveguide was tested with 100 vol.% water and mixture solutions with water content ranging from 0.2 vol.% to 87.5 vol.%. Solution droplet volume used was 1 μL. The temporal variation of transmitted power of the GO-coated optical waveguide during the application of water-alcohol mixture solutions with selected values of water content is included in Fig. 3.

The temporal variation shows two distinct profiles. For water content of more than 30 vol.%, transmitted power would increase by a maximum value of 32 dB before decreasing back to the initial value when the solution droplet was completely evaporated as shown in Fig. 3(a).



(a)



(b)

Fig. 3 Change in transmitted power of the GO-coated waveguide over time when 1 μL of the water-alcohol mixture solution with (a) 30 vol.% – 100 vol.% and (b) 0.2 vol.% – 30 vol.% of water content were applied onto the GO coated optical waveguide.

The time taken for the complete evaporation of solution droplet was linearly related to the water content, as shown in Fig. 4. The time taken for complete evaporation of 1 μL of pure water droplet was 714 seconds, which decreased to 47.5 seconds for 1 μL of water-alcohol solution with 30 vol.% of water content. This corresponded to an increase in about 9.8 seconds to achieve the complete evaporation of the solution droplet with every 1 vol.% increase in water content. Therefore, the "drying time" of a fixed volume of water-alcohol solution could be used to indicate the water content in the mixture solution for water content of more than 30 vol.%.

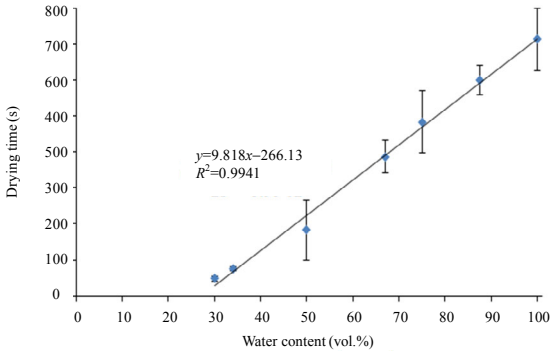


Fig. 4 Change in measured drying time of the GO-coated waveguide when the water-alcohol mixture solution with water content between 30 vol.% and 100 vol.% was applied.

On the other hand, when water-alcohol mixture solutions with water content of 25 vol.% or less were applied on the GO coating, the transmitted power remained low initially before increasing to a maximum achievable transmitted power level. This was then followed by a decrease in transmitted power to its initial value when the mixture solution was completely evaporated, as shown in Fig. 3(b). The initial insignificant response of the proposed sensor could be explained by the filtration characteristic of GOF where larger alcohol molecules were not able to permeate into the GO coating. In addition, the amount of free water molecules in a water-alcohol mixture solution was smaller than those in the total water content because water tended to form complex bondings with alcohol molecules [23–25]. Over the drying period, IPA evaporated faster than water due to its higher partial pressure compared with water [23, 26]. As a result, increasing amount of water molecules was "freed" from the water-alcohol bonding and were able to permeate into the GO coating, with the effect eventually became large enough to be measured by the proposed sensors. At the same time, the maximum transmitted power measured did not achieve the maximum value as in the case during the measurement by using the mixture solution with water content of 30 vol.% or more. It is believed that the amount of water in the solution was not enough to "saturate" the GO coating and fully reduced its TE-polarized light transmission loss. In this case, the maximum transmitted power attained decreased linearly with decreasing water content. The maximum transmitted power measured decreased from 31 dB to 10.6 dB for the mixture solution with water content of 25.0 vol.% to 0.2 vol.%, respectively, as shown in Fig. 5. The maximum transmitted power measured for water content in this range was calculated to be 0.7485 dB for every 1 vol.% of change in water content, for the application of 1 μL mixture solution droplet. Note that this sensitivity was only applicable for water content of less than 30 vol.% in a 1 μL mixture solution droplet. Also, the measurements above were obtained by using a single GO-coated optical waveguide, which showed that the proposed sensor could be used for repeated measurements instead of single-use only. The calculated value showed that the GO-coated optical waveguide had very high sensitivity to minute amount of water. The large variation in the change in transmitted power will allow the development of high sensitivity water content measurement in water-alcohol solution.

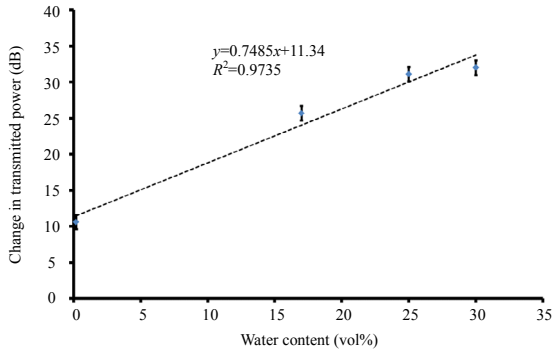


Fig. 5 Change in the maximum transmitted power of the GO-coated waveguide when water-alcohol mixture solution with water content between 0.2 vol.% and 30 vol.% was applied.

4. Conclusions

All-optical water content measurement by using graphene oxide as functional element was demonstrated. The proposed sensor made use of the unique characteristics of graphene oxide film – the variable TE-polarized light transmission loss in the presence of water and its highly selective

permeability. When a water droplet was applied onto the GO-coated optical waveguide, water molecules permeated easily into the GO layers and reduced the TE-polarized light absorption, which led to a significant increase in the transmitted optical power. A reduction in the transmission loss of more than 30 dB was obtained when a water droplet of 1 μL in volume was applied onto the GO-coated optical waveguide and the response was instantaneous. The response of the proposed sensor was tested by using water-alcohol mixture solutions with different water contents. For water content of < 30 vol.%, it was found that the maximum measured transmitted power increased linearly with increasing water content and saturated for water content of > 30 vol.%. For higher water content, the time taken for the restoration of the initial transmission characteristics (drying time) was found to increase linearly with increasing water content, from 30 vol.% up to 100 vol.%. The proposed sensor has a potential for the use in in-situ water content measurement in water-alcohol solutions.

Acknowledgment

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