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Graphene oxide coated long period grating based fibre optic humidity sensor

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ABSTRACT

In this paper, the response of a graphene oxide (GO) coated long period grating (LPG) to the change in temperature and in humidity is reported. To create the probe, an improved Hummer's method was used to synthesis the GO solution used as its basis, allowing coating of functionalized LPG by using a multi-layer dip coating technique. A consistent and stable response of the resonance peak intensity of the GO coated LPG was observed to the change in humidity, achieving a sensitivity of 0.15 dB / %RH with a linear correlation coefficient of 0.9804 over the relative humidity range from 60%RH to 95%RH at room temperature (25°C). A blue shift of the resonance peak wavelength was recorded when the proposed sensor was exposed to varying temperature conditions from 25°C to 70°C and the response was found to be linear with a correlation coefficient of 0.9973. The GO coated LPG humidity sensor probe performed with a good stability and repeatability over a number of test cycles in this initial performance evaluation.

Keywords: humidity sensor, long period grating, graphene oxide, optical fibre

1. INTRODUCTION

Relative humidity (RH) sensors play a significant role in electronic products, the food industry, structural health monitoring and many other storage applications. Optical fibre based humidity sensors have been used in preference to conventional electrical sensors due to their very attractive features such as immunity to electromagnetic interference, multiplexing capability, small size and resistance to many hazardous and corrosive environments [1]. LPGs have been reported as a promising refractive index (RI) sensors due to their high sensitivity to the surrounding RI change compared to the other optical fibre sensors [2]. In LPGs, light propagating in the core interferes with some of the co- propagating cladding modes and thus the resulting resonance bands depend on the effective refractive index of the propagating medium, which comprises of cladding refractive index, as well as the refractive index of the surrounding material around the cladding. This approach is used as the basis of this sensor probe.

Graphene oxide (GO) is the 2D nanomaterial that comprises of many oxygen contained groups such as epoxides and carboxylic groups on a single layered graphene sheet. It is obtained by chemical exfoliation of graphite in a very strong oxidizing agent such as potassium permanganate ($KMnO_4$). Even though GO has been known for quite a long time, it has only attracted attention following the discovery of graphene in 2004 [3]. These oxygenated groups lead to a rich surface chemistry diversity [4] that enables various kinds of physical and chemical interactions with a wide range of chemical and biochemical species, nanoparticles and biostructures, and can be easily dispersed in many aqueous and organic solvents. With interesting features like these, combined with a simple and a low cost synthesis process, GO makes it a very attractive candidate for chemical and biochemical sensors.

In this paper, a fibre optic humidity sensor is presented, that comprises of a GO coated LPG as the essential sensing principle. GO flakes were immobilized on the fibre surface by functionalizing the fibre surface with polymerizable acrylate groups using 3-(trimethoxysilyl)propyl methacrylate before coating GO to achieve a stable performance of the sensor. The transmission spectra of this GO coated LPG are presented over a relative humidity range from 60%RH to 95%RH. The temperature dependency of the sensor is also investigated and analyzed, with a view to providing correction for temperature excursions in the use of the probe.

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2. THEORETICAL BACKGROUND

The minimum transmission of loss bands in a LPG is governed by the equation [5],

$$T_i = 1 - \sin^2(\kappa_i L) \tag{1}$$

where T_i is the minimum transmission of the ith cladding mode, K_i is the coupling coefficient of the ith cladding mode, which is obtained by the overlap integral of the core and cladding mode and by the amplitude of the periodic modulation of the mode propagation constants. L is the length of the LPG in the probe. The RI change induced by the surrounding environment, e.g. the GO coating layer, affects the evanescent field and thus the coupling coefficient, which eventually leads to noticeable intensity changes of LPG loss bands. Any change in the intensity of the resonance attenuation bands can be explained by this phenomenon.

When the coupling conditions are satisfied, forward propagating light in the core mode couples with co-propagating cladding modes at the long period grating. The resonance wavelength λ_{res} can be written as,

$$\lambda_{res} = (n_{core}^{eff} - n_{cladd.m}^{eff})\Lambda_{LPG} \tag{2}$$

where n_{core}^{eff} and $n_{cladd.m}^{eff}$ are the effective refractive indices of fundamental core mode and the mth cladding mode, respectively. Λ_{LPG} is the grating period of the LPG. Based on the above equation, any change in the effective RI of core or cladding will lead to a shift of the resonant loss peak. As mentioned before, the effective refractive index of the cladding mode comprises of the cladding RI as well as the RI of the surrounding material, in this case, GO. Any shift of the resonance peak wavelength can be explained by this phenomenon.

3. SENSOR FABRICATION

A B/Ge co-doped photosensitive fibre was exposed to the light from a 248-nm Krypton Fluoride (KrF) excimer laser with a pulse energy of 8 mJ and a pulse frequency of 100 Hz through a metal amplitude mask with a period of 400 µm to create the 25 mm long LPG. After the inscription process, the LPG was annealed at 180°C for 2 hours to stabilize the sensor performance. An improved Hummer's method was used to synthesize the GO used in this work (detailed procedure can be found in [6]). GO aqueous dispersion used to coat the LPG was prepared by immersing 0.5 mg of prepared GO flakes in 10 mL deionized water and sonicating for 1-hour period. Then the solution was centrifuged at 3000 rpm for 15 minutes. This centrifugation process was carried out three times and the supernatant was taken to achieve a high percentage of single layered GO flakes in the solution. Before coating, the LPG was immersed in a H_2SO_4:H_2O_2 (7:3) solution at room temperature for half an hour, followed by washing with distilled water and drying at 80°C for an hour to clean the coating surface and leave it with exposed hydroxyl groups which facilitate bonding of a silane agent. Afterwards, the LPG surface was functionalized with polymerizable acrylate groups by coating 3-(trimethoxysilyl)propyl methacrylate three times using the dip coating machine (dip duration 120 seconds and drying at 100°C for 3 minutes). GO was then coated on the functionalized LPG surface using the same technique (dip duration 120 seconds and drying at 100°C for 5 minutes - this process was carried out repeatedly until a noticeable coating was achieved on the LPG surface). A microscopic image of the GO coated LPG together with a bare LPG for cross-comparison is represented in Fig 1. A brownish black coating was clearly visible after deposition. The transmission spectrum of the LPG, before and after coating, is illustrated in Fig. 2. These results indicated that GO was successfully coated on the LPG surface in this key fabrication step for the probe.
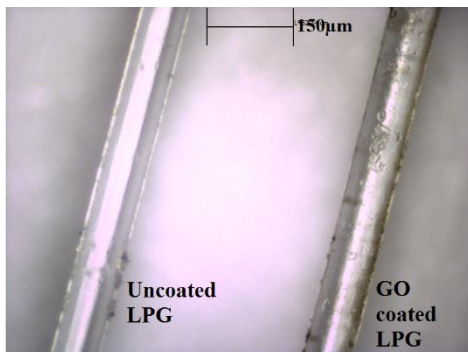

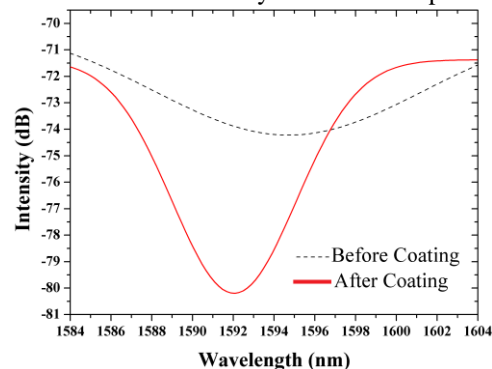Figure 1. Microscopic image of GO coated LPG and a bare LPG

Figure 2. Transmission spectra of the LPG before and after coating

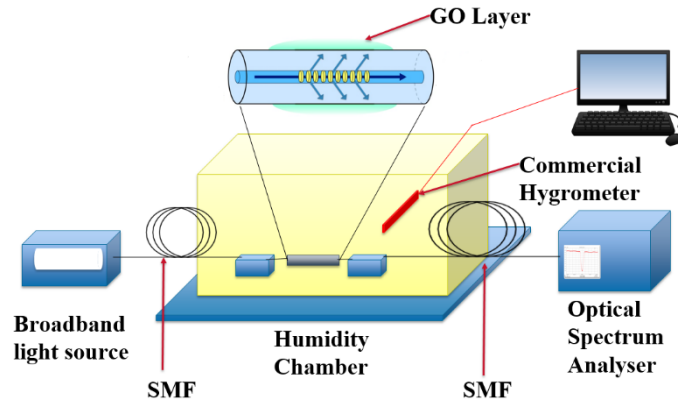## 4. TEMEPERATURE AND HUMIDITY RESPONSE OF GO COATED LPG

Figure 3. Experimental setup

Fig. 3 illustrates the experimental setup used for the evaluation of the sensor performance as a function of humidity and temperature changes. One end of the GO coated LPG was connected (via SMF-Single Mode Fibre) to a broadband light source (OceanOptics LS1) and the other end was connected to an optical spectrum analyzer (Yogokawa AQ6370C) to record the transmission spectra. In doing so, the GO coated LPG was mounted on two stages (as shown in Fig. 3) inside the humidity chamber (Binder KBF 115) to minimize the errors caused by external strain and bending effects. The humidity chamber is capable of rapid changes of relative humidity in the range of 5%RH to 95%RH at a certain temperature value (25°C to 100°C). The system was allowed to stabilize before the transmission spectra was recorded at each humidity level. A commercial hygrometer was used to calibrate the temperature and the relative humidity of the chamber for these tests.
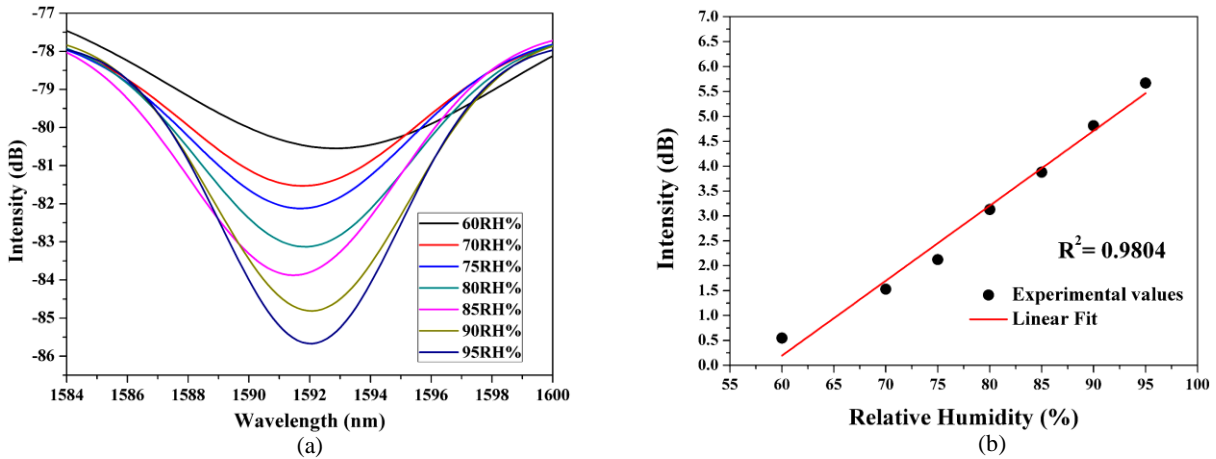

Figure 4. (a) Transmission spectra of GO coated LPG at different relative humidity levels; (b) Intensity variations of the resonance peak at 1592 nm at different relative humidity levels

To observe the humidity response of the sensor, the temperature of the humidity chamber was initially fixed at 25°C and the relative humidity level was changed from 20%RH to 95%RH. Fig. 4 (a) illustrates the transmission spectra of the resonance peak of GO coated LPG at a wavelength of 1592 nm for various humidity levels. A minimal intensity or peak wavelength shift was observed for lower humidity levels but beyond 60%RH, it was clearly observed that with increasing humidity levels, the intensity of the resonance peak was increased with a slight shift of the peak wavelength. The active response range of 60%RH to 95%RH agrees well with the performance of a reported reduced GO based humidity sensor [7]. GO is super-permeable to water molecules and when moisture molecules are present inside the GO material, it leads to a change of optical properties of GO such as the RI and coupling coefficient and hence the change of peak wavelength and intensity of the resonance loss band. Fig.4 (b) depicts the intensity change of the resonance peak at 1592 nm with varying RH levels. The peak intensity of -80.54 dB and -85.66 dB were recorded at 60%RH and 95%RH, respectively. A good linear correlation between RH levels and the peak intensity was observed with a linear correlation coefficient of 0.9804. This leads to a RH sensitivity of 0.15 dB/%RH over the range of 60%RH to 95%RH at 25°C.
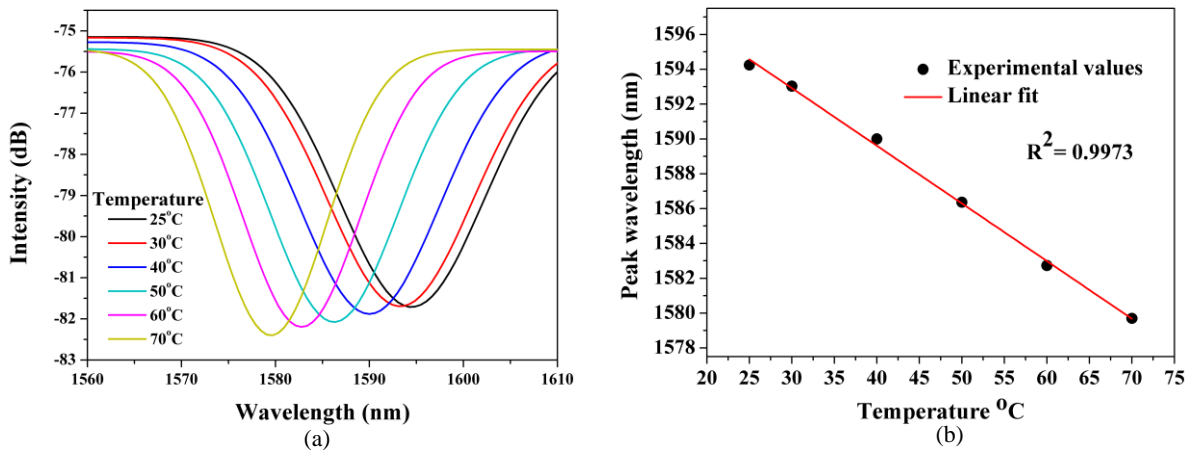
Figure 5. (a) Transmission spectra of GO coated LPG at different temperature levels; (b) Wavelength of the resonance peak at different temperature levels

The effect of temperature on the sensor probe was investigated by fixing the relative humidity level at a modest 45%RH and changing the temperature from 25°C to 70°C. Fig. 5 (a) represents the transmission spectra of the resonance peak at various temperature levels while Fig.5 (b) depicts the wavelength shift of the same resonance peak with varying temperature conditions. The peak wavelengths of 1594.24 nm and 1579.69 nm were recorded at 25°C and 70°C, respectively. A very good linear correlation between the temperature change and the peak wavelength shift was observed with a temperature sensitivity of 0.32 nm/°C and a linear correlation coefficient of 0.9973. A slight change of the peak intensity (0.6dB) was observed when the temperature was increased from 25°C to 70°C. The peak wavelength shift recorded against temperature changes could be used for effective temperature measurement thus for temperature compensation of the humidity sensor developed.

5. CONCLUSION

A novel approach to a humidity sensor probe has been presented, based on a GO coated LPG by exploiting the super permeability of GO to water molecules and its dependency of thermo-optic properties in the presence of water molecules. An improved Hummer's method was used for GO synthesis and 3-(trimethoxysilyl)propyl methacrylate was coated on the LPG surface to immobilize coated GO flakes to achieve a stable sensor performance. A satisfactory linear response of the humidity sensor was recorded over the 60%RH to 95%RH humidity range with a sensitivity of 0.15 dB / %RH at 25°C. A good linear correlation between temperature and the peak wavelength shift was also observed for a temperature range of 25°C to 70°C. The sensor performed with a consistent repeatability and stability. Based on these results, we would like to present GO as a very attractive sensing material for optical fibre sensors that will be investigated further. Future work will include increasing the sensitivity by varying the RI of the GO solution as well as experimenting with the coating thickness.

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