Graphene oxide for improved sensitivity and response time of fibre Bragg grating-based humidity sensors

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ABSTRACT

We report on the characterisation of relative humidity sensors based on fibre Bragg gratings coated with two hygroscopic materials: polyimide (PI) and graphene oxide (GO). In both cases, sensitivity and response time could be tuned by varying the coating thickness, but graphene oxide provided significantly higher sensitivity and a faster response time than polyimide: for PI-coated sensors, a 1 pm/% increase in sensitivity resulted in a 94 s increase in response time, whereas for GO-coated sensors, the same increase in sensitivity only cost an additional 1 s increase in response time. These results show that graphene oxide is a promising material for faster-responding humidity sensors that can maintain high sensitivity.

Keywords: fibre optic sensors, relative humidity, fibre Bragg gratings, polyimide, graphene oxide, response time

1. INTRODUCTION

Measurement of relative humidity (RH) is of high importance to many industrial applications, including gravity sewers infrastructure monitoring [1] [2][[3], leak detection in nuclear power plants [4], condensation detection in cooled systems [5] and concrete manufacturing [6]. Fibre-optic based sensors are well-suited to humidity sensing at nearly 98-99 % RH, due to their resistance to gaseous corrosion and high biofouling, as well as other harsh environmental conditions such as radiation and temperature extremes. Fibre Bragg gratings (FBGs) coated with hygroscopic material are a common approach, in which the coating material expands and contracts in response to changes in ambient RH, applying a strain to the FBG [7]. Since the peak reflected wavelength of the FBG is proportional to strain, the peak wavelength shift may be calibrated to relative humidity.

Many hygroscopic coating materials have been proposed, including polyimide [8], agar [9], organo-silica hybrid materials [10], graphene oxide [11] [12] and combinations of these materials [13], with a range of sensitivities and response times reported. For most coatings, sensitivity is dependent on coating thickness, due to a larger volume of absorbed water generating greater expansion. However, this creates a trade-off between sensitivity and response time, since a thicker coating also leads to a slower response to RH changes [8] [9] [14]. Graphene oxide is highly hydrophilic, with a large surface area that facilitates rapid adsorption and desorption of water molecules, offering the possibility of rapid responses to humidity changes while maintaining high sensitivity.

In this study, we have investigated the relationship between sensitivity and response time of FBG -based humidity sensors based on two hygroscopic coatings: polyimide (PI) and graphene oxide (GO), with a range of coating thicknesses, comparing the performance of these coatings side by side.

2. METHODS

FBGs were inscribed in photosensitive single mode fibre (SM1500(4.2/125), Fibercore), using the phase mask method with an excimer laser (Atlex FBG, wavelength 248 nm, 5 mJ pulse energy, 5 ns pulse duration, 50 Hz pulse repetition rate, and 15 s exposure time). The inscribed FBGs were 6 mm in length, with an average peak reflectance of 70% and peak

wavelengths between 1500 nm and 1600 nm. Following inscription, the fibres were annealed in an oven at 180 °C for 4 hours. After annealing, the FBGs were coated with either polyimide (PI-2525, HD Microsystems) or graphene oxide.

For PI coating, the FBGs were first coated with a bonding agent (3-aminopropyl triethoysilane, Sigma-Aldrich). The polyimide coating was applied using dip coating, with either 10, 15 or 20 layers of polyimide, at a coating speed of 0.1 mm/s, and heat curing for 5 minutes at 150 °C between each layer. After all layers were deposited, the coated FBGs were further heat-cured in an oven at 180 °C for 1 hour.

The graphene oxide (GO) suspension for coating was prepared using Hummer's method with a concentration of 15 mg/ml. The GO was coated to FBGs using a typical dip-coating process. We confirmed the integrity of the coating of GO formed on the FBG with Raman spectroscopy. The thickness of coated GO layers was controlled from ~10 to 20 μm and confirmed using both optical microscope and scanning electron microscope.

The coated fibres were spliced with single mode LC/APC pigtails and connected to a fibre-optic sensor interrogator (Hyperion si155, Luna Inc.), which recorded the peak reflectance wavelengths at a sampling rate of 0.1 Hz. The coated FBGs were placed in an environment chamber (KMF 115, Binder) and fixed horizontally, ensuring no strain was placed on the FBGs. The humidity in the environment chamber was varied from 20% RH to 80% RH, with steps of 10% RH and a duration of 2 hours for each step. The temperature was fixed at 40 °C. This cycle was repeated three times. At each humidity step, 50 data points near the end of the step were averaged. Sensitivity coefficients for the sensors were obtained by linear fitting of the mean wavelengths versus RH data, with the gradients of the fitted lines corresponding to the sensitivity coefficients (pm/%) for the sensors.

The speed of response of the RH sensors to a sudden change in humidity was estimated by fitting the wavelength data recorded during the transition from 40% RH to 50% RH, to the theoretical expression for the step response of a first-order instrument [15]:

$$\lambda = K_H H_{step}\left(1 - \exp\left(-t/\tau\right)\right)$$

Where λ is the peak reflected wavelength, K_H is the humidity sensitivity coefficient, H_{step} is the size of the step change in humidity (10% in this case), t is the time in seconds, and τ is the time constant in seconds, or the time for the signal to reach 63.2% of its final value (minus starting value). The fitted parameter τ was used to compare response times of the PI and GO coated sensors.

3. RESULTS

The wavelength shifts (measured wavelength minus the initial wavelength at the start of the measurement) during the calibration cycle for representative PI-coated and GO-coated sensors are shown in Figure *1*(a). The wavelength shift was linear with RH for both coating types, as shown by the calibration curves in Figure *1*(b), and the GO-coated sensor had a higher sensitivity compared to the PI sensor (28.4 pm/% and 10.3 pm/% respectively). The range of sensitivity coefficients measured was 7.7 pm/% to 28.4 pm/% for GO, and 0.8 pm/% to 11.8 pm/% for PI. A small drift in the wavelength can be seen at 80% RH for the GO-coated sensor.

The response times of the GO-coated sensors were significantly shorter than those of the PI-coated sensors, as can be seen in Figure *1*(c), with time constants of 32 s and 899 s respectively; across all sensors tested, the time constants ranged from 12.8 s – 38.4 s for GO, and 16.8 s – 1126.5 s for PI. Plotting the time constant against sensitivity for all sensors tested with both coating types (Figure *1*(d)) shows a linear relationship between time constant and sensitivity for both coating types, indicating a trade-off between these two performance metrics; however, the relative increase in time constant for a given increase in sensitivity (i.e. the gradients of the lines these data lie on) is much larger for PI than for GO: based on linear fits, the PI-coated sensors exhibit a 94 s increase in time constant for a 1 pm/% increase in sensitivity, while for the GO-coated sensors, the increase in time constant for a 1 pm/% increase in sensitivity is 1 s.

4. CONCLUSIONS

In this study, we compared the sensitivity and response time for two types of relative humidity sensor, both based on fibre Bragg gratings coated with hygroscopic materials. The use of graphene oxide improved both the sensitivity and response times compared with polyimide, by increasing the diffusion rate of the water that causes expansion of the hygroscopic coating, as measured by the strain on the FBG. For both coating types, a linear relationship was found between time constant and sensitivity; however, the constant of proportionality is almost 100 times larger for GO than for PI, revealing

GO to be a highly promising material for both rapid and sensitive RH measurement. The time constant vs sensitivity curve provides a useful metric for comparing the performance of these two hygroscopic FBG coatings, and could be extended to other coating materials and material parameters such as porosity [9]. While previous studies have shown that sensitivity and response time can be optimized for different applications by controlling the coating thickness, our results show that the relationship between these parameters can be dramatically different for different materials, with PI and GO offering almost entirely separate parameter spaces for both sensitivity and response time. The performance and life of the new sensors will be validated in a suitable highly corrosive environment, with relative humidity > 95%. It will then be possible to identify researchable gaps to convert these sensors into an industrial technology.

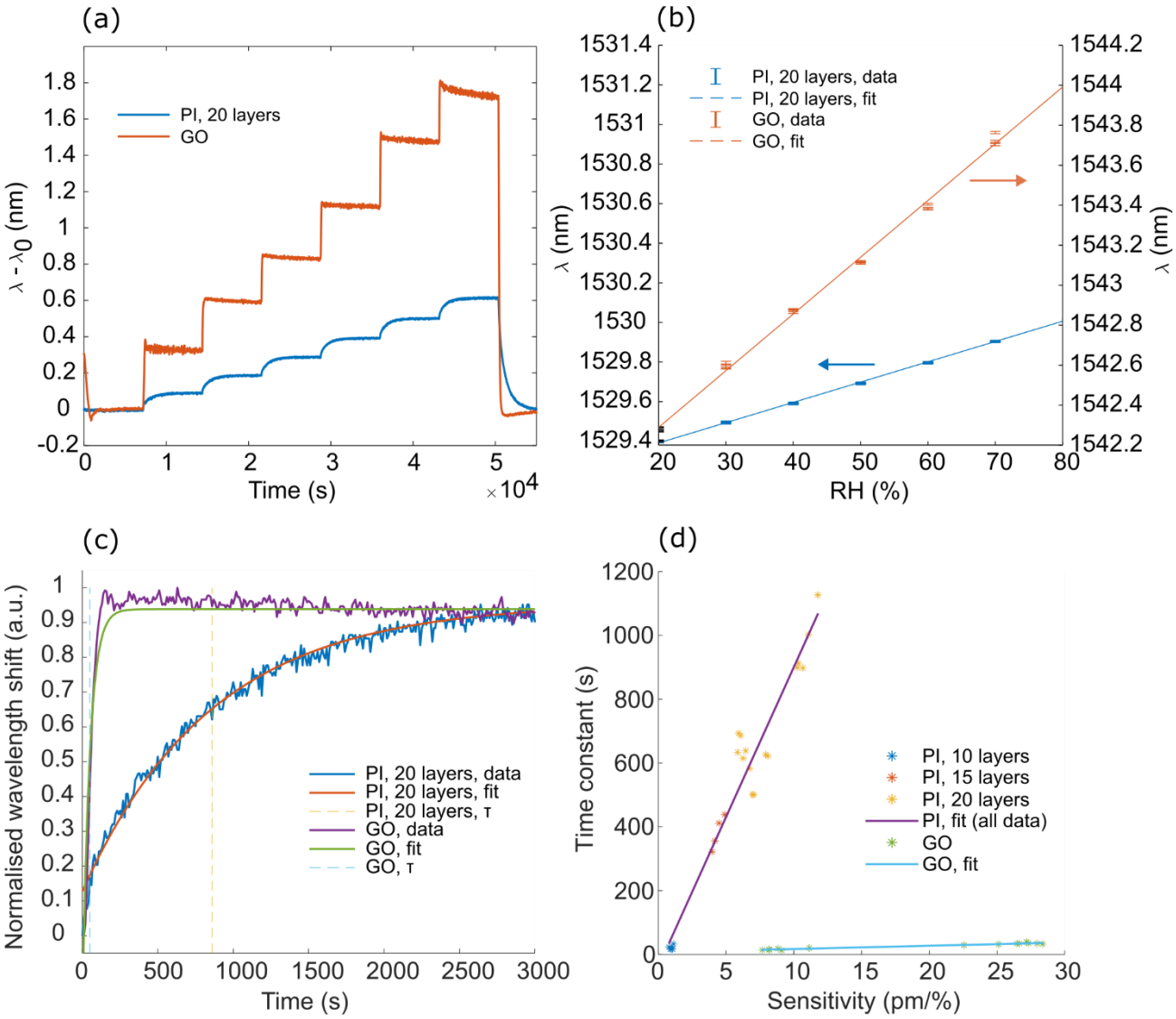

Figure 1: (a) Wavelength shift (initial wavelength λ0 subtracted) versus time for representative polyimide (PI) and graphene oxide (GO) coated relative humidity (RH) sensors during calibration with RH steps from 20% to 80%; (b) Calibration curves obtained from the data shown in (a) for PI and GO sensors; (c) Wavelength data, baseline-subtracted and normalized, versus time during a step change from 40% RH to 50% RH, with fitted lines used for estimating the time constant τ; (d) Time constant versus RH sensitivity coefficient for PI and GO coated sensors, showing data for all sensors tested.

ACKNOWLEDGEMENTS

The authors acknowledge the funding support of Sydney Water and the material assistance provided by Integrated Civil and Infrastructure Research Centre, which was part funded by EPSRC Grant EP/R010420/1. Tongxi Lin and Xiaojun Ren acknowledge the UNSW University International Postgraduate Award Scholarship.

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