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Graphene oxide-coated microbottle resonators for relative humidity sensing

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Graphene oxide (GO) is a 2D coating material used to improve fiber optics sensors' response to relative humidity. Microbottle resonators (MBRs) have garnered more attention as sensing media structures. An MBR with a 190 μm diameter was coated with GO. Then, tapered fiber light coupling was used to investigate the relative humidity sensing performance in the range of 35—70%RH at 25 °C. The MBR showed a higher Q factor before and after GO coating. The sensitivity of 0.115 dB/%RH was recorded with the 190 μm GO-coated MBR sample compared to a sensitivity of 0.022 dB/%RH for the uncoated MBR sample. These results show that the MBR can be used in fiber optic sensing applications for environmental sensing.

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Humidity monitoring is vital for industrial production. Resistive and capacitive humidity sensors have a limited range of operation in temperature and frequency. Fiber optics sensors have the advantages of compactness, remote sensing abilities, adequate corrosion resistance, and immunity to electromagnetic interference[1]. The fiber structure is usually modified to achieve light leakage and allow interaction with the environment. Tapering[2], side-polishing[3,4], and microresonators[5-8] are typical for environmental sensing.

Microbottle resonators (MBRs) have a high Q factor and low free space range (*FSR*)[5,9-11]. High-quality factors are needed to ensure light coupling between the tapered fiber and the resonator. *FSR* contributes to the dynamic range of the sensing setup. Thus, sensing resonators with these qualities showed improved performance[12,13]. Polymer-based MBRs with graphene oxide (GO) coating were shown to have a sensitivity of 0.161 nm/%RH[14]. However, high-temperature annealing is needed, and microbottles preparation using polymers with UV irradiations can be more complex than using the method of soften-and-compress. Uncoated microbottle elements have been used to measure relative humidity and showed a sensitivity of 0.048 7 dB/%RH in the range of 40—80%RH[15] and used for formaldehyde and sodium hypochlorite sensing[8,16,17].

In our previous works, agarose-coated MBRs were shown to have a sensitivity of 0.107 7 dB/%RH[18]. Hydroxyethyl cellulose/polyvinylidene fluoride (HEC/PVDF)-coated MBRs have a sensitivity of 0.111 dB/%RH[19]. Preparation and maintenance of HEC/PVDF coatings were challenging. The agarose-coated samples needed careful handling to avoid damaging the coatings. Using GO was the next step to achieve good sensing performance with more straightforward preparations and maintenance.

Because of their large surface-to-volume ratio, 2D materials, such as GO, phosphorous, and transition metal dichalcogenides, are used for relative humidity sensing. These materials have shown good sensitivity and resolution when used to detect relative humidity changes[20]. GO is a 2D honeycomb-structure material. GO has large functional groups containing oxygen (-COOH and -OH) bonded covalently on the boundaries between layers. Thus, GO has hydrophilicity and dispersibility.

Water molecules help to maintain the layers' structure of the GO layer through the interaction between the hydrogen bonds in the water molecules and the oxygen in

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the GO's epoxy group. Van der Waals forces cause the water molecules to be absorbed on the surface of the GO coating[21-23]. As the relative humidity increases, the GO layers absorb more water molecules, increasing the layers' distances and changing the coating's refractive index[3,24,25]. Thus, changes in the ambient relative humidity affect the light propagation characteristics of GO-coated fiber sensors. GO can be produced with low-cost setups. GO has been adopted as an active material for relative humidity[23]. Tab.1 shows examples of GO coated fiber sensors.

Tab.1 Examples of relative humidity sensors using GO

Sensing structure	Relative humidity range (%RH)	Sensitivity
Tilted fiber Bragg grating (TFBG)	10—80	0.129 dB/%RH[25]
In-fiber Mach-Zehnder interferometer	60—77	0.349 dB/%RH[26]
Micro-nano fiber Bragg grating (MFBG)	20—80	17.361 pm/%RH[23]
Side-polished single-mode fibre	32—85	0.145 nm/%RH[3]

MBRs should be characterized to examine their sensitivity to refractive index changes in the ambient environment. MBRs can be characterized by the harmonic oscillator's truncated profile[5]. MBRs can be used for refractive index sensing since the resonance wavelength is affected by the surrounding media. Refractive-index-sensitive whispering gallery modes (WGMs) can circulate on the resonator's surface and show as spectra transmission dips. A shift happens in the dips of the transmission spectra in response to refractive index changes in the surroundings. The sensitivity is obtained by dividing the total wavelength shift by the total refractive index. Making MBR is a promising option for sensing applications, showing sensitivity for refractive index changes up to ~150 nm/RIU[10]. Meanwhile, GO is a 2D honeycomb-shaped material with large functional groups containing oxygen (-COOH and -OH) bonded covalently on the layers' boundaries[21-23]. On the surface of the GO, more active carriers adsorb water molecules and cause charge transfer between the molecules and the GO[3,24,25]. Thus, the presence of water molecules (the analyte) in the ambient surroundings affects the light propagation characteristics of GO-coated MBR sensors.

The microbottles were prepared by the soften-and-compress technique and a manual fusion splicer (Furukawa Electric Fitel S178A). The soften-and-compress technique was chosen for several reasons. The technique provides reliable, stable bubble forming. The number of arcs controls the bulging size. The splicer machine provides positioning controls to form symmetrical shapes. Repeating the same bubble-forming steps (positioning and number of arcs) produced similar MBR dimensions. We used the splicer machine with our lab microscope to ensure the resonator samples used in all the experiments had similar dimensions. Our lab setup was built for this resonator preparation method.

An intact single-mode fiber (SMF) was placed inside the splicing platform. SMF was our current scope of work. This splicer applied plasma arcs while compressing the two edges of the cable. The combined effect of the compressing and the arcs create a bubble formation. The resonator is characterized by the bottle diameter, stem diameter and bottle length[20], as shown in Fig.1. The number of arcs applied by the splicer controls the MBRs' diameter. In this work, MBR samples with 190 μm diameter were prepared.

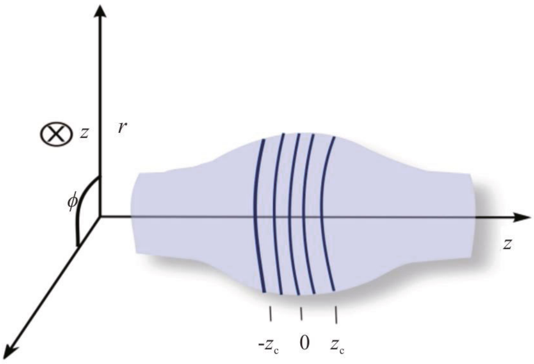


Fig.1 MBRs dimensions

GO dispersion from the vendor graphenea was sonicated by the sonication machine for 24 h. The sonication machine was used without excessively heating the solutions. Afterward, the microbottle samples were submerged in the solution and kept there for 1 h. The samples were left in the oven for 3 h at 35 °C. The coated samples were left for 24 h before the experiment. It should be noted that the thickness of the GO film was adjusted and optimized by controlling the concentration of the GO solution and the immersion time.

Fig.2 shows the experimental setup. A tunable laser source (TLS ANDO AQ4321D) was used, because it provides a wide range of wavelengths with a fine resolution of 0.001 nm. This light was coupled into the micro-bottle samples via tapered fiber. The flame-brushed tapered fiber was prepared on SMF. A 3 μm diameter tapered fiber was used because this diameter size was adequate to couple light into the microfiber. Smaller diameters were too fragile to withstand the steps of the experiment. Larger diameter sizes have smaller evanescent fields limiting the amount of coupled light into the resonator.

The TLS provides a narrow line-width light through the tapered fiber, and the light is detected using an optical power meter (THORLABS PM100D). The sensing structure was placed inside a humidity chamber. The relative humidity was controlled between 35—70%RH using a saturated salt solution (sodium hydroxide). Each sample was tested in the controlled relative humidity chamber at a constant temperature of 25 °C and pressure of 1 atm repeatedly for three cycles of operation. Environmental disturbances were avoided by sealing the chamber throughout the experiment. The sensing setup was secured with UV adhesive on the workbench. The experiment setup was left undisturbed for the experiment duration. The experiment room was temperature and humidity controlled. Our current scope and experiment setup is SMF, but we hope to expand to other fiber types.

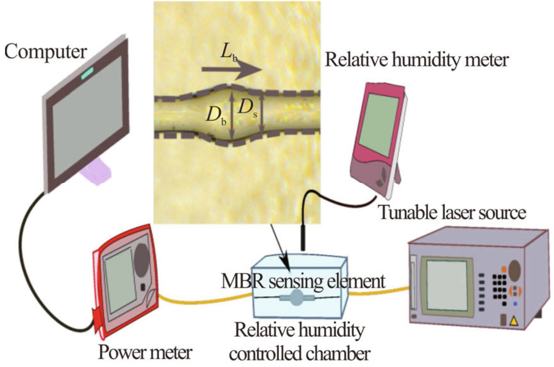


Fig.2 Experimental setup for the proposed sensor

Fig.3 shows the transmission modes of the microbottles samples before and after being coated with GO. The uncoated MBR samples showed a Q factor higher than 5×10^5. The GO-coated MBR samples showed a Q factor higher than 2.5×10^5. The coatings on the MBR resonators affect the light coupling efficiency and impact the Q factor of the resonators. However, the Q factor remains higher than 10^5.

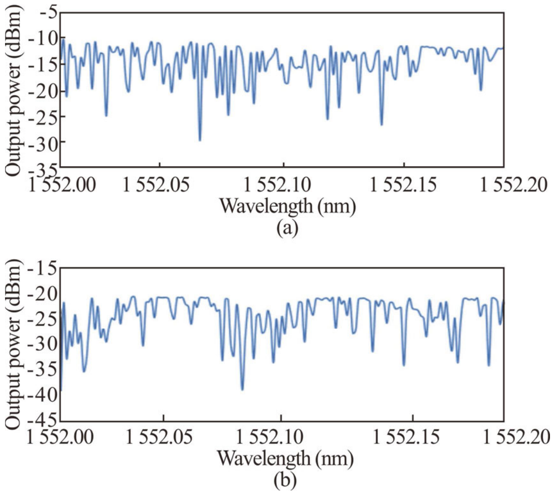


Fig.3 Transmission modes of the coated microbottle samples WGM: (a) Uncoated MBR; (b) GO coated MBR

The output power variations in response to changing relative humidity are recorded in Fig.4. The microbottle samples show increasing loss when relative humidity changes between 35—75%RH because of the scattering loss caused by water particles and the GO responding to relative humidity changes. In previous works, GO responded to changes in relative humidity by changes in its layers' thickness and refractive index[20]. The increasing thickness of the GO layers due to the water molecules in higher relative humidity impacts the coupling between the tapered fiber and the MBR[16,24,25] and impedes the light coupling between the resonator and the tapered fiber limiting the losses of the fiber that would occur in lower humidity levels. When the coated MBR samples are exposed to higher humidity, the GO coating absorbs moisture from the air, causing swelling in the coating of the resonator. Thus, limiting the amount of light that couples into the resonator causes more light to pass through the tapered fiber and higher detected light output power. The uncoated MBR samples showed a sensitivity of 0.022 dB/%RH compared to 0.115 dB/%RH for the samples with GO coating. All the samples showed linearity higher than 90%. The GO-coated samples showed a linearity higher than 99%.

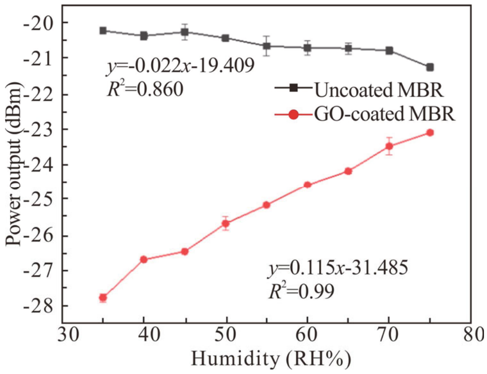
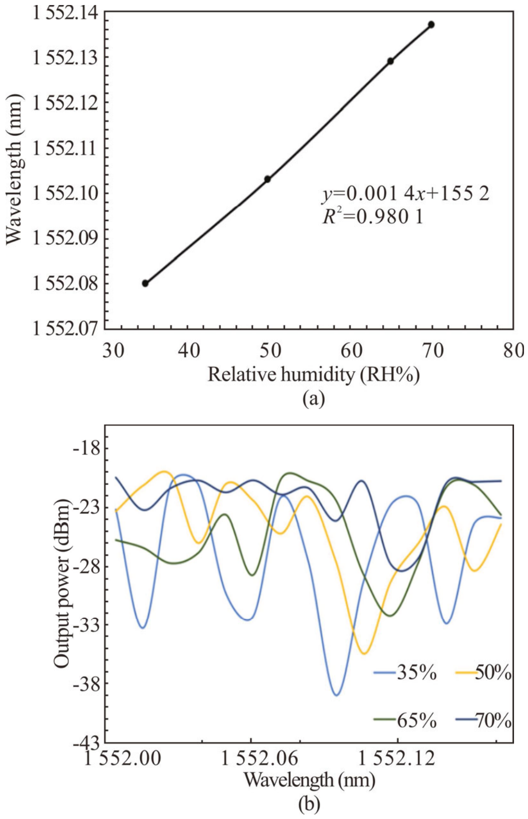


Fig.4 Light power changes with relative humidity for the MBR samples

The coated microbottle samples' WGM transmission responses at different relative humidity levels are shown in Fig.5(a). The GO coating absorbs these water molecules and the refractive index changes. Fig.5(b) shows a narrow range of wavelengths for clarity. The figures became hectic when wider wavelength ranges were chosen due to the light coupling between the tapered fiber and the resonator. Fig.5(b) shows that the light coupling at a low relative humidity of 35%RH is stronger due to water absorption into the GO layers at higher relative humidity. Thus, lower relative humidity figures show more resonance dips. The GO thickness increases with higher relative humidity and the material's refractive index changes, thus changing the light coupling conditions into the resonator and causing a resonance shift. The response of the resonance shift reaches a sensitivity of 1.4 pm/%RH, as shown Fig.5(a).

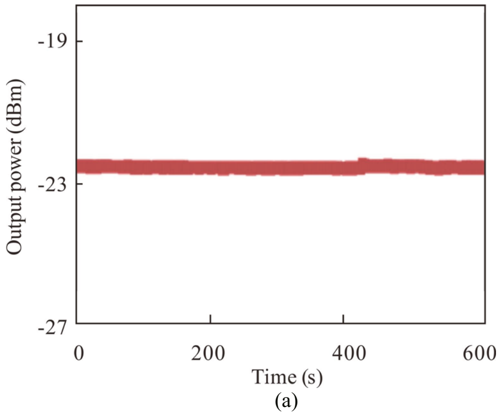


(a)

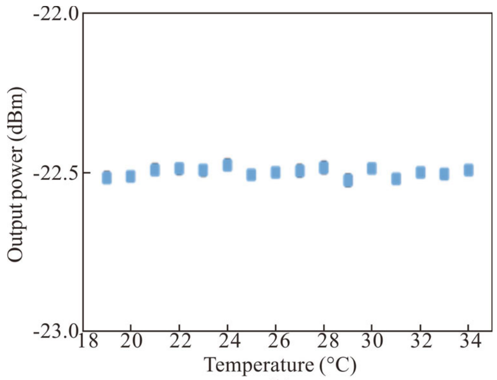
(b)

Fig.5 (a) Response of the coated sensor; (b) Transmission spectra of the GO-coated sensor

The stability of this sensing structure is studied in Fig.6. The sensing element was placed in the controlled chamber, and the output power variations were recorded for 300 s at a constant relative humidity of 65%RH. The temperature was constant at 25 °C for this stage. Monitoring the light output levels during humidity detection was of interest to ensure that the graphene coating absorbing water molecules from the air is consistent. Temperature effect needed to be investigated for this sensor. The temperature range of 19—34 °C is a range that the currently available setup can reliably provide. The response of the light output levels was recorded at a relative humidity of 65%RH for 5 min at each temperature value. The sensor showed no fluctuation with temperature changes in this range, as seen in Fig.6(b).



(a)



(b)

Fig.6 The stability of the GO-coated MBR sample with (a) time and (b) temperature

Fig.7 shows several cycles of the proposed sensor response to relative humidity changes in the range of 35—75%RH. This setup was necessary to study the response cycles of the coated sensor. The cycles show the repeatability of the sensor response to relative humidity changes. The experiment was conducted by switching the sensor from a controlled chamber of 75%RH to 35%RH, which was the room's relative humidity. This switch takes less than 1 s using silica gel pellets, a valve, and a small wireless fan. The light output change was recorded. The average response time was 5 s to these changes. For the current experiment setup, the investigated relative humidity range was 35—75%RH. We hope in the future to expand the testing range to lower and higher values.

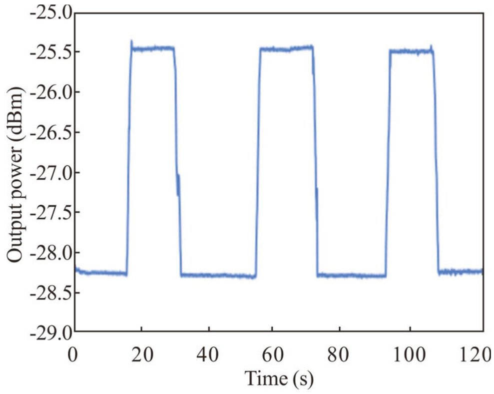


Fig.7 Response cycles of the proposed sensor

Tab.2 shows the sensing performance of the MBR samples. The sensitivity is higher for the GO-coated MBR at 0.115 dB/%RH. All samples show linearity higher than 90%. However, the GO-coated sensor showed a higher linearity higher than 99%. The standard deviation and the resolution of the coated MBR sample were 0.094 dBm and 0.820%RH, respectively, showing the advantage of using a GO coating due to GO's hydrophilicity. The average limit of detection for the GO-coated samples was 2.46%RH. The proposed sensing structure was able to respond to changes in relative humidity.

Tab.2 Sensing parameters of the sensors

Parameters	Uncoated MBR	GO-coated MBR
Sensitivity (dB/%RH)	0.022	0.115
Standard deviation (dBm)	0.149	0.094
Resolution (%RH)	6.789	0.820
Linearity (%)	92.736	99.499

This paper discusses the effect of GO on microbottles for humidity detection. An MBR was prepared using the heat-and-compress method with SMF. Then, GO coating was applied to the MBR sample. A 3 μm diameter tapered fiber was used for coupling light. The microbottle samples' Q-factors were higher than 10^5. The performance of these samples was investigated, and the output power was measured in the relative humidity range of 35—75%RH. The GO-coated MBR sensor showed a better sensitivity of 0.115 dB/%RH than the uncoated sample, with a sensitivity of 0.022 dB/%RH. The GO-coated samples showed improved standard deviation and resolution due to GO's hydrophilicity.

Ethics declarations

Conflicts of interest

The authors declare no conflict of interest.

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