PMMA microfiber coated with ZnO nanostructure for the measurement of relative humidity

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Abstract. PMMA microfibers coated with zinc oxide (ZnO) nanostructure are demonstrated for relative humidity monitoring. The fabrication of two different microfiber structures, namely the straight PMMA microfiber and the PMMA microfiber loop resonator (PMLR) were performed by using the direct drawing technique. The sensitivities of the PMMA microfibers were compared and analyzed. The results implied that the PMLR is more sensitive than the straight PMMA microfiber and the sensitivity of the sensors were further increased with the additional coating of ZnO nanostructure on the surface of the PMMA fiber.

Keywords — polymethyl methacrylate (PMMA), PMMA microfiber, relative humidity, zinc oxide nanostructure

1. Introduction
Over the last two decades, fiber optic sensors have been gaining popularity among research institutions and industries. The fiber optic sensor technology offers the ability to accomplish multiplexing capabilities, remote sensing, versatility, improved performance, high sensitivity and can easily operate under strong electromagnetic field conditions. They also offer multiple possibilities for combining a large number of different sensors (e.g., those used for detecting temperature, pH, humidity, high magnetic field, displacement, pressure and acceleration) into the same optical fiber, thus eliminating the need for multiple cables as required in traditional electronic sensing [1].

Recently, optical microfibers have been demonstrated to be useful in sensor applications including temperature, pH, concentration of molecules and humidity due to its interesting optical properties. An evanescent field is created around the decreased microfiber diameter of several micrometers, enabling 50% of the power guided through it to propagate outside the physical microfiber. This evanescent field is able to offer high light intensity due to strong confinement and is especially beneficial for sensing the surrounding that comes into contact with it. By exploiting these properties, low-cost, miniaturized and all-fiber based optical devices for various applications [2] could be developed. Furthermore, these optical microfibers have shown to be promising for the development of various...
kinds of micro- and nanophotonic components and devices [3-4]. Typical microfiber-based sensing structures, including the simple straight microfiber and the microfiber loop resonator have been widely used. The former can be directly fabricated by using the heat pulling method while the latter can be easily maintained by van der waals or electrostatic forces at the joint area [5]. Embedding the microfiber loop inside a polymer is another possible route to fabricate a robust micro-resonator for sensing applications [6-8].

Zinc oxide (ZnO) is an attractive, relevant and biosafe material and can be use as a sensing element. It has a wide band gap of 3.3eV at room temperature and may be integrated into a wide range of nanoscale devices such as optoelectronic devices, surface acoustic wave devices, piezoelectric devices, transparent conducting materials, solar cell and field emitters. In addition, ZnO nanostructures are one of the most promising materials for the fabrication of chemical and biosensors due to its exotic and versatile properties including biocompatibility, nontoxicity, chemical and photochemical stability, high specific surface area, optical transparency, electrochemical activities, high electron communicating features and so on [9-11]. Growing ZnO nanostructure on flat substrates has been extensively demonstrated in various platforms such as glass, silica and aluminium foil [12-14]. Recently, it has been reported that ZnO nanostructure enhances the interaction of fiber guided light for humidity sensor [15].

Here, a straight PMMA microfiber and a PMMA microfiber loop resonator (PMLR) were fabricated by direct drawing the solvated polymer. The smooth morphology of PMMA microfibers make them suitable for low loss optical wave guiding and sensing. Furthermore, PMMA optical fibers are low cost polymer fibers that are generally more physically robust and flexible than silica fibers [16]. In this paper, the straight PMMA microfiber and the PMLR were coated with ZnO nanostructure for detecting changes in relative humidity. The ZnO nanostructure coating on the microfibers induces changes to the optical properties in response to an external stimulus.

2. Methodology
Firstly, a silica tapered fiber was fabricated through a tapering process at high temperature known as flame brushing technique. This technique was able to fabricate the silica microfiber with good accuracy. Figure 1 shows a schematic illustration of the silica microfiber fabrication setup using oxy butane burner as a torch. Through this technique, the diameter of the heated glass can be reduced when the single mode fiber is stretched by two fiber holders. An amplified spontaneous emission (ASE) source is injected into one end of the single mode fiber while the other end is connected to an optical spectrum analyzer (OSA) to monitor the transmission spectrum of the silica microfiber during the fabrication process.

Figure 1. Schematic illustration of the silica microfiber fabrication setup.
Next, a PMMA microfiber was fabricated using direct drawing technique. The PMMA microfiber with a diameter of 6 microns was fabricated by using a one-step process as illustrated in Figure 2. PMMA was selected as the polymer wave-guiding material due to its high mechanical strength, good dimensional stability, good weather resistance, and its natural transparency above the deep ultraviolet region. A heating plate was used to melt PMMA and keep the temperature constant during the fiber drawing process. First, the tip of fabricated tapered silica fiber with a diameter of about 125 μm was immersed into the molten PMMA. Then the fiber tip was retracted from the molten polymer with a speed of 0.1−1 m/s, leaving a PMMA microfiber extending between the molten PMMA and the tip. The extended PMMA microfiber was quickly quenched in air and subsequently forming a bare PMMA microfiber. The microfiber diameter can be controlled by the pulling speed and viscosity of the polymer (which depends on the hot plate temperature). Microfibers produced by this technique are uniform in diameter over a long length with good flexibility.

![Figure 2. Schematic diagram of the PMMA microfiber fabrication setup.](image)

As for the ZnO nanostructure, the seed layer was deposited onto the fiber to grow the ZnO nanostructures using a simple manual dip coating technique. The seeded solution was prepared by dissolving zinc acetate dehydrate (Zn(CH₃COO)₂•2H₂O) as a precursor in isopropanol with a molarity of 0.025 M. The solution was stirred at 60° C for 2 hours at ambient temperature to yield a clear and homogenous solution. Then, the solution was cooled down to room temperature for the coating process. The fiber was manually dipped into the seeding solution and dried at 30°C to evaporate the solvent repeatedly for 5 times to increase the thickness of the fiber during the coating and drying process. Subsequently, the growing solution was prepared by dissolving 0.01M zinc nitrate hexahydrate (Zn(NO₃)₂•6H₂O) and 0.01M hexamethylenetetramine (HMTA) in 100ml deionized water. The deposition process of ZnO nanostructure on the fibers was performed using sol-gel immersion method by suspending the ZnO fibers in the growing solution at 30°C for 2 hours. The fiber was then characterized using Field Emission Scanning Electron Microscope (FESEM) to investigate the morphology of the ZnO nanostructure coated onto the PMMA microfiber (see Figure 3).

The setup used to measure relative humidity is shown in Figure 4. The amplified spontaneous emission (ASE) light from the Erbium-doped fiber amplifier (EDFA) was launched into the microfiber probe placed in a sealed chamber with a dish filled with saturated salt solution. The transmitted light was measured by the optical spectrum analyzer (OSA). In the experiment, the performance of the proposed sensor was investigated for various level of relative humidity. The output power was measured against the relative humidity ranging from 20% to 80% in steps of 5% using the omega RH-21 C temperature-relative humidity meter.
3. Results and discussion
Figure 5 shows the microscope image of the straight PMMA microfiber and the PMLR with a PMMA microfiber diameter and loop diameter of 6 µm and 56 µm, respectively. As shown in Figure 5, the input and output ends of the PMLR are aligned to each other. The alignment was made possible due to the surface attraction force of electrostatic and Van der Waals, which kept the ends of the PMMA to stick to each other. The van der Waals attraction force between the two adjacent PMMA microfiber is strong enough to withstand the elastic force from the bended microfiber and maintain the microfiber loop structure. Figure 6 shows the comb transmission spectrum of the PMLR, which was obtained by using an ASE source in conjunction with an OSA. The extinction ratio is about 1.0 dBm.
During the experiment, the measurements were recorded throughout the relative humidity range of 20% to 80%. Figure 7 shows the output of the uncoated straight PMMA microfiber against relative humidity. The linearity, sensitivity and resolution of the sensor was obtained at 97%, 0.117 dBm/% and 8.41 %, respectively. The sensitivity refers to slope of the linear curve whereas the resolution was obtained from the ratio of the standard deviation to the sensitivity of the sensor (refer Table 1).
Figure 7. The output power of the ASE against relative humidity for the uncoated straight PMMA microfiber.

Table 1. The performance of the humidity sensor using the uncoated straight PMMA microfiber.

| Parameter                  | Value  |
|----------------------------|--------|
| Sensitivity (dBm/%)        | 0.117  |
| Linear Range (%)           | 20-80  |
| Linearity (%)              | More than 97% |
| Standard Deviation (dBm)   | 0.985  |
| Resolution (%)             | 8.41   |

In Figure 8, the output power of the straight PMMA microfiber coated with the ZnO nanostructure is plotted against the relative humidity. It is observed that the output power increases with the increase in the relative humidity. The sensitivity of the slope is 0.1439 dBm/% for the output power versus relative humidity within the -14.55 dBm/% to -5.13 dBm/% range and a standard deviation of 0.945 dBm obtained from repeated measurements. The ZnO nanostructure coating has increased the sensitivity of the sensor 23%, hence improving its resolution by 22%. The ZnO composite that are
exposed to humid environment cause a rapid surface absorption of water molecules. The increase in the water molecules cause an increase in both the effective refractive index of the surrounding medium and the absorption coefficient of the ZnO composite, leading to larger leakage of light [17].

![Graph showing the output power of the ASE against relative humidity for the straight PMMA microfiber coated with ZnO nanostructure.](image)

**Figure 8.** The output power of the ASE against relative humidity for the straight PMMA microfiber coated with ZnO nanostructure.

**Table 2.** The performance of the humidity sensor using the straight PMMA microfiber coated with ZnO nanostructure.

| Parameter                  | Value  |
|----------------------------|--------|
| Sensitivity (dBm/%)        | 0.1439 |
| Linear Range (%)           | 20-80  |
| Linearity (%)              | More than 99% |
| Standard Deviation (dBm)   | 0.945  |
| Resolution (%)             | 6.57   |
Figure 9 depicts the output power obtained from the uncoated PMLR for various relative humidity levels. The performance of the relative humidity sensor is summarized in Table 3. Similar to the previous results, it is observed that an increase in the relative humidity level can be detected by an increase in the output power. The sensitivity and the resolution are 0.137 dBm/% and 7.88%, respectively.
Table 3. The performance of the humidity sensor using the uncoated PMLR.

| Parameter                  | Value                |
|----------------------------|----------------------|
| Sensitivity (dBm/%)        | 0.137                |
| Linear Range (%)          | 20-80                |
| Linearity (%)              | More than 97%        |
| Standard Deviation (dBm)   | 1.08                 |
| Resolution (%)             | 7.88                 |

Figure 10 shows the output power obtained from the ZnO coated PMLR against the relative humidity. The performance of the relative humidity sensor is summarized in Table 4. The sensitivity and the resolution are 0.178 dBm/% and 6.045 %, respectively. It is observed that the coating of the ZnO nanostructure is able to increase the sensitivity of the sensor by 30%, hence improving the sensor’s resolution by 23%. In general, the PMLR outperforms the straight PMMA microfiber in terms of its sensitivity and resolution. This is because the PMLR induces more portion of the evanescent wave outside of the microfiber, enabling more interaction with the relative humidity.
Figure 10. The output power of the ASE against relative humidity for the PMLR with ZnO nanostructure coating.

Table 4 The performance of the humidity sensor using the PMLR with ZnO nanostructure coating.

| Parameter               | Value     |
|-------------------------|-----------|
| Sensitivity (dBm/%)     | 0.178     |
| Linear Range (%)        | 20-80     |
| Linearity (%)           | More than 99% |
| Standard Deviation (dBm)| 1.076     |
| Resolution (%)          | 6.045     |
4. Conclusion
A simple humidity sensor based on the straight PMMA microfiber and the PMLR have been successfully demonstrated within the range of 20% to 80%. In comparison, when the PMLR is used instead of the straight PMMA microfiber, an improvement in the sensitivity and resolution of the sensor was observed. It is observed that coating of the ZnO nanostructure is able to further increase the sensitivity of the sensor hence improving the sensor’s resolution. The coating of sensitive material onto the tapered fiber has successfully enhanced the performance of the microfiber as a humidity sensor.

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