Tapered Plastic Optical Fiber Coated With Al-Doped ZnO Nanostructures for Detecting Relative Humidity

Zuraidah Harith, Ninik Irawati, Hartini Ahmad Rafaie, Malathy Batumalay,
Sulaiman Wadi Harun, Roslan Md Nor, and Harith Ahmad

***Abstract*— A relative humidity (RH) sensor is demonstrated using a tapered plastic optical fiber (POF) that is coated with Al-doped ZnO nanostructures. A simple etching method was used to fabricate the tapered POF that operates based on intensity modulation technique. The tapered fiber was then coated with Al-doped ZnO nanostructures using sol–gel immersion method with different mol% of Al nitrate that acts as a dopant. The 1 mol% of Al nitrate that used in the synthesis process exhibited better performance compared with the other doping concentrations. Then, results obtained for both undoped ZnO and 1 mol% of Al-doped ZnO were compared and investigated. The performance of 1 mol% of Al-doped ZnO demonstrated better linearity and sensitivity of 97.5% and 0.0172 mV/%, respectively, whereas the undoped ZnO yielded linearity and sensitivity of 93.3% and 0.0029 mV/%, respectively. The proposed sensor provides numerous advantages, such as simplicity of design, low cost of production, higher mechanical strength, and is easier to handle compared with silica fiber optic. Results show that tapered POF with Al-doped ZnO nanostructures enables the increase in sensitivity of fiber for detection of changes in RH.**

***Index Terms*— Al-doped zinc oxide, fiber optic sensor, tapered plastic optical fiber, relative humidity (RH) sensor.**

I. INTRODUCTION

PLASTIC Optical Fiber (POF) has been developed and commercialized in various applications including sensors due to its characteristics that make it greater in flexibility and resistance to impacts and vibrations as well as greater coupling of light from light source to fiber [1]. As the principle of operation is based on an optical signal, they also exhibit immunity to electromagnetic interference [2]. POF-based sensor was chosen because it does not require sophisticated materials, is easily automated, can be operated at room temperature and is capable of handling varying pressure conditions. POF consists of cladding and core with refractive index of 1.402 and 1.492 respectively. The cladding of the POF was removed using a chemical etching technique. This was done so that Al-doped ZnO nanostructures can be coated onto the tapered region. ZnO was chosen because it is a wide band gap semiconductor with a gap energy of about 3.4 eV at room temperature, and regularly used as transparent conductive layer without toxic components [3]. It is also a unique material that exhibits semiconducting, piezoelectric, and pyroelectric multiple properties. These unique nanostructures unambiguously demonstrate that ZnO is probably the richest family of nanostructures among all materials, both in structures and properties [4]. When aluminium (Al) is doped with ZnO, the electrical property of ZnO is improved and the optical or magnetic properties can be altered [5]. ZnO can be doped with various Group-III metals such as B, Al, In and Ga, among which Al doping produces highly conductive due to the close covalent bond length of Al–O (0.192 nm) to that of Zn–O (0.197 nm) [6].

The need to sense moisture in moisture-sensitive environments such as semiconductor manufacturing and packaging has become essential. For the humidity sensor, the sensing mechanism is based on the adsorption and desorption process, and the surface area reaction with the water vapor to determine the sensing properties. To date, a number of evanescence wave sensors have been demonstrated for humidity measurement. As an instance, Muto et al. demonstrated a humidity sensor which is based on reversible absorption of water (H_2O) from the ambient atmosphere into a porous thin-film interferometer that sits on the tapered fiber and the water absorbed changes the refractive index of the thin films and subsequently transform the lossy fiber into a light guide [7]. In another study, Gaston et al. (2003) demonstratedfiber-optic sensors based on the interaction of the evanescent field in side-polished standard single mode fibers with the external medium or overlay. In order to detect changes in relative humidity, suitable material that could readily absorb and desorb water

Manuscript received May 5, 2014; revised August 21, 2014; accepted August 21, 2014. Date of publication September 4, 2014; date of current version November 25, 2014. This work was supported by the University of Malaya under Grant UM.C/625/1/HIR/MOHE/SCI/29 and in part by INTI International University under Grant INT-FOSTEM-04-01-2014. The associate editor coordinating the review of this paper and approving it for publication was Dr. Anna G. Mignani.

Z. Harith is with the Institute of Graduate Studies, University of Malaya, Kuala Lumpur 50603, Malaysia, and also with INTI International University, Nilai 71800, Malaysia (e-mail: zuraidah.harith@newinti.edu.my).

N. Irawati is with the Institute of Graduate Studies, University of Malaya, Kuala Lumpur 50603, Malaysia (e-mail: ninixchermie@gmail.com).

H. A. Rafaie and R. M. Nor are with the Department of Physics, University of Malaya, Kuala Lumpur 50603, Malaysia (e-mail: tinie5636@gmail.com; rmdnor@um.edu.my).

M. Batumalay and S. W. Harun are with the Department of Electrical Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia (e-mail: malathy.batumalay@newinti.edu.my; swharun@um.edu.my).

H. B. Ahmad is with the Photonics Research Center, University of Malaya, Kuala Lumpur 50603, Malaysia (e-mail: harith@um.edu.my).

Color versions of one or more of the figures in this paper are available online at http://ieeexplore.ieee.org.

Digital Object Identifier 10.1109/JSEN.2014.2353038

was coated on the surface. Another side polishing method has been reported by Ribeiro (2002) and it is stated that the coarser polishing leads to stronger surface light scattering, allowing measurements of refraction index smaller than the fiber cladding value. Xu.et al demonstrated an optical-fiber humidity sensor based on phenomenon of evanescent wave scattering. A porous polymer coated on the top of an optical-fiber core scatters the evanescent wave and attenuates the light intensity guided in the fiber [9]. Chen et al., (2012) also presented a relative humidity fiber sensor based on Fabry–Perot interferometry configuration. The proposed fiber sensor is functionalized with a thin layer of a moisture-sensitive natural polymer chitosan to form a low fineness Fabry–Perot sensor. The sensing scheme used in this work is based on the swelling effect of chitosan sensing film (degree of swelling varies as a function of relative humidity) which will induce optical path modulation when relative humidity is changed. Another example is a sensor fabricated using a $CoCl_2$ doped thin polymer film coated on the bare fiber core by Khijwania et al. (2005). The fiber optic relative humidity (RH) sensor was based on the evanescent wave absorption spectroscopy using a single U-bend plastic-clad silica fiber with high dynamic range and high sensitivity. The cladding of the plastic-clad silica multi-mode fiber was removed from the central portion of the fiber and a highly humidity sensitive film then deposited. As the light at a wavelength close to the peak absorption wavelength of the sensing film propagates through the sensing region, the optical power in evanescent tail of the propagating mode is absorbed with the change in the environmental parameter (humidity). This results in a modulated output from the fiber, which is used as the criterion for detecting and determining the relative humidity in the surrounding environment [11]. Other than that, Batumalay et al. has proposed a humidity sensor that was coated with ZnO nanostructures using sol-gel immersion method on ZnO seeded and non-seeded fiber whereby the ZnO nanostructures that are exposed to an environment of humidity causes rapid surface adsorption of water molecules and changes in optical properties, and the seeding technique causes an increase in both effective refractive index of surrounding medium and absorption coefficient of the ZnO nanostructures surfaces, thus leads to larger leakage of light [12]. In this work, POF was tapered and coated with Al-doped ZnO nanostructures and its behavior towards changes in relative humidity based on the intensity modulation technique was studied.

II. EXPERIMENT

The tapered POF is prepared based on the chemical etching technique using acetone, de-ionized water and sand paper. The POF used has an overall cladding diameter of 1 mm, a numerical aperture of 0.51 and an acceptance angle of 61°. The refractive index of the core and cladding are 1.492 and 1.402 respectively. The acetone was applied to the POF using a cotton bud and neutralized with the de-ionized water. The acetone reacted with the surface of the polymer to form milky white foam on the outer cladding which was then removed by the sand paper. This process was repeated until the tapered fiber has a stripped region waist diameter of 0.45 mm. In an earlier work, it was found that tapers with waist diameters in the range of 0.40 mm to 0.50 mm showed good sensitivity to refractive index variation whereas those with waist diameters above 0.55 mm and below 0.40 mm did not demonstrate substantial sensitivity [13]. The total length of the tapered section was 10 mm. Finally, the tapered POF fibers were cleansed again using de-ionized water. These tapered plastic fibers were then coated with Al doped ZnO nanostructures.

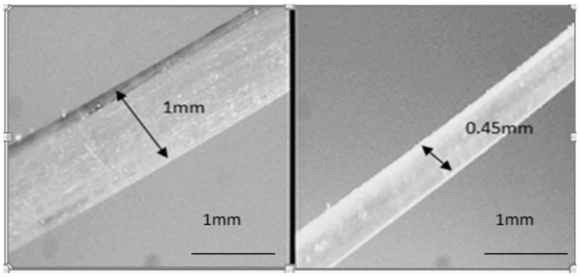
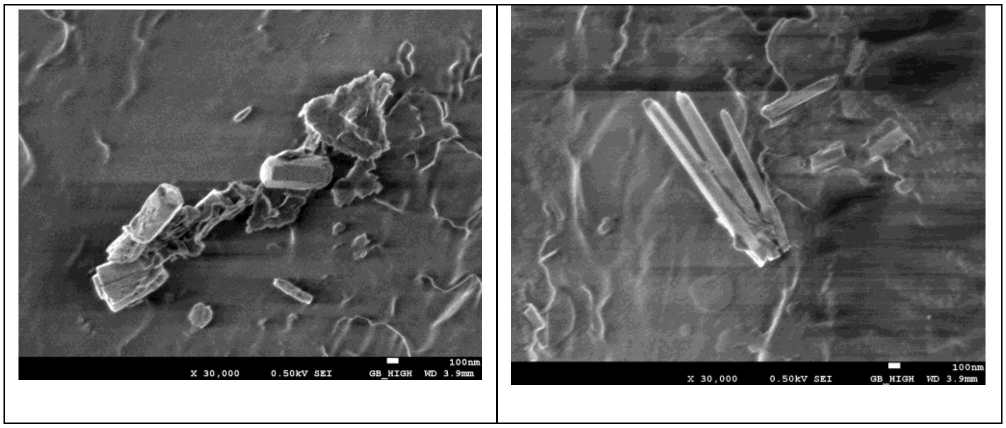


Fig. 1. (a) and (b) Shows the microscope images of the original un-tapered, tapered POF, which have a cladding diameter of 1 mm and 0.45 mm respectively.

The un-doped ZnO and 1 mol% Al-doped ZnO nanostructure were synthesized using the sol–gel method. Aqueous solution of zinc nitrate hexaydrate ($Zn(NO_3)_2.6H_2O$ (0.01 M), hexamethylenetetramine (HMTA; C6H12N4] (0.01 M) and aluminum nitrate nonahydrate ($Al(NO_3)_3.9H_2O$) are prepared using deionized (DI) water. The solution was stirred until solution temperature rose to 60 °C for 2 hours to obtain clear homogeneous solution and then the solution was kept for aging for 24 hours prior for fiber coating process. The fiber was put in the solution for 15 hours. Finally the fibers were taken out of solution and cleaned with DI water and dried at 50°C. The fiber was then characterized using Field Emission Scanning Electron Microscope (FESEM) to investigate the morphology of undoped and Al-doped ZnO nanostructures coated tapered fiber.

Fig. 1(a) and (b) show the microscope images of the original un-tapered, tapered POF, which have a cladding diameter of 1 mm and 0.45 mm respectively. Fig. 2 shows the FESEM images of ZnO nanostructures (Fig.2(a)) and Al doped ZnO nanostructures (Fig.2(b)). From the pictures, it can be seen that the morphology of ZnO will change when it is doped with aluminium. It has been proved and reported by Djurišić et al [5].

Fig. 3 shows the experimental setup for the proposed sensor to detect changes in relative humidity using the fabricated tapered POF with un-doped ZnO and Al-doped ZnO nanostructures. The setup consists of a light source, an external mechanical chopper, the proposed probe, a highly sensitive photo-detector, a lock-in amplifier and a computer. The input and output ports of the tapered POF are connected to the laser source and photo-detector, respectively. The light source used in this experiment is a He-Ne laser which operates at a wavelength of 633 nm with an average output power of 5.5 mW. It was chopped at a frequency of 113 Hz by a mechanical chopper to avoid the harmonics from the line frequency which is about 50 to 60 Hz. The 113 Hz frequency



(a) (b)

Fig. 2. Shows the FESEM images of un-doped ZnO nanostructures (Fig.2(a)) and Al doped ZnO nanostructures (Fig.2(b)).

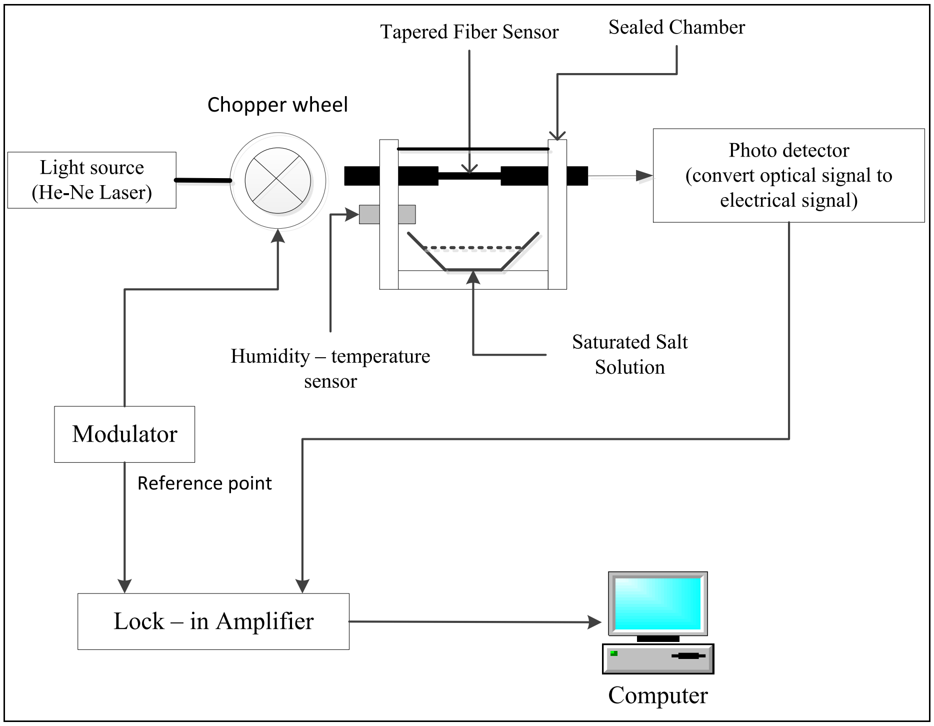


Fig. 3. Experimental setup for the proposed relative humidity sensor using a tapered POF coated with un-doped ZnO and Al-doped ZnO nanostructures.

was chosen as an odd number to prevent multiplication of 50 and 60 Hz. Besides that, it is an acceptable value of output and stability. In addition to that, an increase to the value of chopper frequency causes the output voltage and stability to decreases. The setup used to measure relative humidity using the fabricated tapered POF coated with un-doped ZnO and Al-doped ZnO nanostructures. Laser source (He-Ne) is launched into the tapered POF placed in a sealed chamber with a dish filled with saturated salt solution. The sealed chamber is constructed with a hole and the tapered POF is introduced through it into the sealed receptacle and suspended to saturated salt solutions in order to simulate different values of relative humidity. In the experiment, the performance of the proposed sensor was calibrated for relative humidity ranging from 50 to 80% using 1365 data logging humidity-temperature meter. The output lights were sent into the silicon photo-detector (818 SL, Newport) and the electrical signal was fed into the lock-in amplifier (SR-510, Stanford Research System) together with the reference signal of the mechanical chopper. The output that resulted from the lock-in amplifier was connected to a computer through an RS232 port interface and the signal was processed using Delphi software. The reference signal from the chopper was matched with the input electrical signal from the photo-diode. This allows a very sensitive detection system that will remove the noise generated by the laser source, photo-detector and the electrical amplifier in the photo-detector.

III. RESULTS AND DISCUSSIONS

Fig. 4 shows the variation of the transmitted light from the tapered POF coated with Al-doped ZnO nanostructures at different doping concentration and the data of output voltages against the relative humidity, which were collected

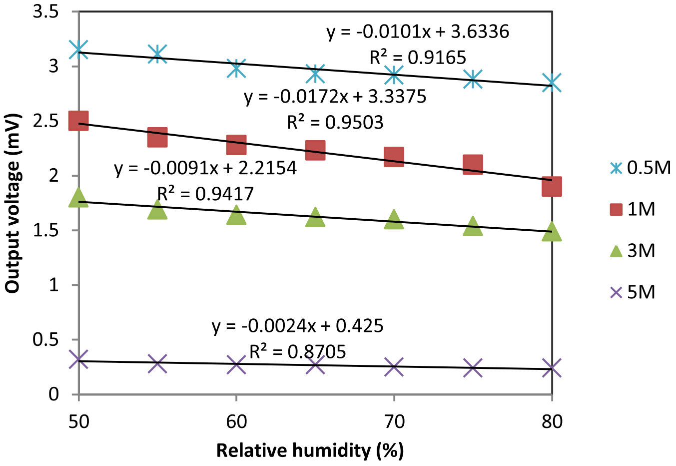


Fig. 4. Output voltage against relative humidity for the proposed tapered POF with Al-doped ZnO nanostructure at different doping concentration.

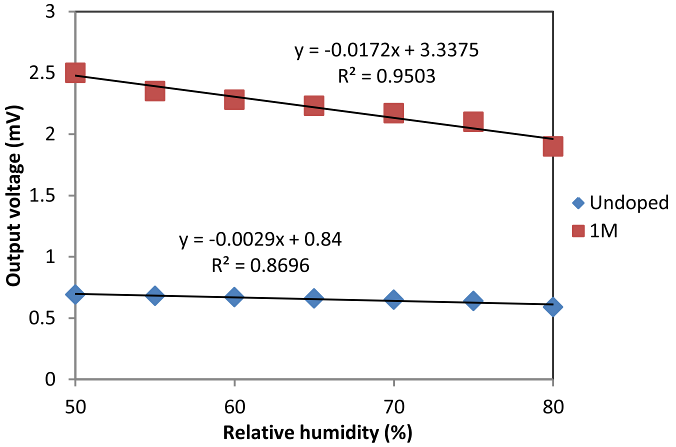


Fig. 5. Output voltage against relative humidity for the proposed tapered POF with un-doped ZnO and Al-doped ZnO nanostructure.

TABLE I

Performance of the Proposed RH Sensor at Different Doping Concentration

Performances	**0.5 mol %**	**1 mol %**	**3 mol %**	**5 mol %**
Sensitivity	*0.0101 mV/%*	***0.0172 mV/%***	*0.0091 mV/%*	*0.0024 mV/%*
Linearity	*95.7 %*	***97.4 %***	*97 %*	*93.3 %*

TABLE II

The Performance of the Proposed RH Sensor for Un-Doped ZnO and Al-Doped ZnO

Performances	***Undopped***	***1 mol %***
Sensitivity	*0.0029 mV/%*	*0.0172 mV/%*
Linearity	*93.3 %*	*97.5 %*
Standard deviation	*0.0789 mV*	*0.0130 mV*
Limit of detection	*13.84 %*	*0.7558 %*

for 600 seconds. The change in the intensity of the transmitted light of the tapered POF coated with Al-doped ZnO nanostructures decreases linearly with relative humidity. It is found that at 1 mol %, the tapered POF has a sensitivity of 0.0172 mV % and a linearity of 97.5 %. These two values are the best amongst the other doping concentrations that were tested in this experiment. Therefore, it can be concluded that tapered POF coated with Al doped ZnO nanostructures at 1 mol % exhibits better performance compared to 0.5, 3 and 5 mol % respectively.

The tapered POF coated with Al-doped ZnOnanostructures at 1 mol 1% is then compared with un-doped ZnO by Batumalay et al. (2014) as shown in Fig. 5. It can be observed that when ZnO is doped with Al, the sensitivity of the proposed sensors have improved as shown in Fig. 5. According to Liu et al., the refractive index (RI) of ZnO composite varies from 1.698 to 1.718 with relative humidity change from 10 – 95% [14]. The ZnO composite are exposed to an environment of humidity which causes rapid surface adsorption of water molecules. The optical properties of ZnO composite surfaces are modulated by the surface adsorption of water molecules. The increase of water molecules being absorbed on ZnO composite results in an increase of relative humidity [14]. The increasing water molecules cause an increase in both effective refractive index of surrounding medium and absorption coefficient of the ZnO composite surfaces and leads to larger leakage of light. In addition, according to Prajapati et al, when ZnO is doped with Al, refractive index will decrease [15]. This decrement causes the graph to decrease; however, the performance of the sensor has enhanced, as shown in Fig. 5. Doping can increase a current carrier in material, therefore when ZnO is doped with Al, there will be more electrons because Al atoms are ionized to Al^{3+} whereas Zn is ionized to Zn^{2+} [16]. Thus one free electron is produced from one Zn atom replacement. The increase in carrier concentration causing a decrease in the resistivity, hence more current can pass through the fiber and therefore yield a higher output voltage.

The performances of the proposed sensor are summarized in Table 1 and Table 2. Overall, the sensor is observed to be sufficiently stable with standard deviations of 0.0130 mV for Al-doped ZnO at concentration of 1 mol % as being recorded for the time duration of 600 s. In comparison, Al-doped ZnO has higher sensitivity than un-doped ZnO. Besides that, when ZnO is doped with Al, the limit of detection has also improved tremendously. The limit of detection (LOD) is calculated by dividing the standard deviation with the sensitivity, which indicates that the system is more efficient when the value of LOD is lower. Based on the calculation, it shows that when ZnO is doped with Al, the sensor is more stable with a value of 0.7558%. These results show that the proposed sensor coated with Al-doped ZnO nanostructures exhibits better performance in measuring the changes of relative humidity in real time.

IV. CONCLUSION

Simple sensor is demonstrated using a tapered POF coated with Al-doped ZnO nanostructures for detecting the changes in relative humidity. The tapered POF was fabricated by an etching method using acetone, sand paper and de-inozed water to achieve a waist diameter of 0.45 mm and tapering length of 10 mm. The tapered fiber is coated with un-doped ZnO and Al-doped ZnO nanostructures with different mol % concentration. It was found that Al-doped ZnO with 1 mol % concentration exhibited better performance. The performance of the fibers was then investigated and it is found that, when ZnO is doped with Al, the performance improves significantly. The output voltage of the sensor using tapered POF coated with Al-doped ZnO nanostructures decreases linearly with better sensitivity of 0.0172 mV/%and slope linearity of 97.5% compared to un-doped ZnO with sensitivity and linearity of 0.0029 mV/% and 93.3% respectively. The electrical properties of the material for Al-doped ZnO is improved as there will be more electrons hence lowering the resistivity of the material, therefore more current can pass through the fiber and yield higher output voltage.

REFERENCES

[1] J. Zubia and J. Arrue, "Plastic optical fibers: An introduction to their technological processes and applications," *Opt. Fiber Technol.*, vol. 7, no. 2, pp. 101–140, 2001.

[2] L. Bilro, N. Alberto, J. L. Pinto, and R. Nogueira, "Optical sensors based on plastic fibers," *Sensors*, vol. 12, no. 9, pp. 12184–12207, 2012.

[3] C. Major *et al.*, "Optical and electrical characterization of aluminium doped ZnO layers," *Appl. Surf. Sci.*, vol. 255, no. 21, pp. 8907–8912, 2009.

[4] W. Gao and Z. Li, "Nanostructures of zinc oxide," *Int. J. Nanotechnol.*, vol. 6, nos. 3–4, pp. 245–257, 2009.

[5] A. B. Djurišić, A. M. C. Ng, and X. Y. Chen, "ZnO nanostructures for optoelectronics: Material properties and device applications," *Prog. Quantum Electron.*, vol. 34, no. 4, pp. 191–259, 2010.

[6] S. Mridha and D. Basak, "Aluminium doped ZnO films: Electrical, optical and photoresponse studies," *J. Phys. D, Appl. Phys.*, vol. 40, no. 22, pp. 6902–6907, 2007.

[7] S. Muto, O. Suzuki, T. Amano, and M. Morisawa, "A plastic optical fibre sensor for real-time humidity monitoring," *Meas. Sci. Technol.*, vol. 14, no. 6, pp. 746–750, 2003.

[8] R. M. Ribeiro, J. L. P. Canedo, M. M. Werneck, and L. R. Kawase, "An evanescent-coupling plastic optical fibre refractometer and absorptionmeter based on surface light scattering," *Sens. Actuators A, Phys.*, vol. 101, nos. 1–2, pp. 69–76, 2002.

[9] L. Xu, J. C. Fanguy, K. Soni, and S. Tao, "Optical fiber humidity sensor based on evanescent-wave scattering," *Opt. Lett.*, vol. 29, no. 11, pp. 1191–1193, 2004.

[10] L. H. Chen *et al.*, "Chitosan based fiber-optic Fabry–Pérot humidity sensor," *Sens. Actuators B, Chem.*, vol. 169, pp. 167–172, Jul. 2012.

[11] S. K. Khijwania, K. L. Srinivasan, and J. P. Singh, "An evanescent-wave optical fiber relative humidity sensor with enhanced sensitivity," *Sens. Actuators B, Chem.*, vol. 104, no. 2, pp. 217–222, 2005.

[12] M. Batumalay *et al.*, "Tapered plastic optical fiber coated with ZnO nanostructures for the measurement of uric acid concentrations and changes in relative humidity," *Sens. Actuators A, Phys.*, vol. 210, pp. 190–196, Apr. 2014.

[13] S. W. Harun, M. Batumalay, A. Lokman, H. A. Rahman, and H. Ahmad, "Electrostatic charge interaction: A case study on tapered PMMA fiber for calcium nitrate detection," *Sensor Rev.*, vol. 34, no. 4, p. 13, 2014.

[14] Y. Liu, Y. Zhang, H. Lei, J. Song, H. Chen, and B. Li, "Growth of well-arrayed ZnO nanorods on thinned silica fiber and application for humidity sensing," *Opt. Exp.*, vol. 20, no. 17, pp. 19404–19411, 2012.

[15] C. S. Prajapati, A. Kushwaha, and P. P. Sahay, "Effect of Al dopants on the structural, optical and gas sensing properties of spray-deposited ZnO thin films," *Mater. Chem. Phys.*, vol. 142, no. 1, pp. 276–285, 2013.

[16] N. D. Md Sin, M. F. Kamel, R. I. Alip, Z. Mohamad, and M. Rusop, "The electrical characteristics of aluminium doped zinc oxide thin film for humidity sensor applications," *Adv. Mater. Sci. Eng.*, vol. 2011, Jun. 2011, Art. ID 974906.

Zuraidah Harith received the B.E. degree in electrical and electronic engineering from University Science Malaysia, Penang, Malaysia, in 2001, and the M.Eng. degree in electrical - electronic and communication engineering from the Universiti Teknologi Malaysia, Johor Bahru, Malaysia, in 2006. She is currently pursuing the Ph.D. degree in photonics with the University of Malaya, Kuala Lumpur, Malaysia. Her current research interests include tapered plastic fiber-based optical sensors and coating of nanoparticles.

Ninik Irawati received the B.E. degree in biomedical engineering from the University of Airlangga, Surabaya, Indonesia, in 2012. She is currently pursuing the master's degree in photonics with the University of Malaya, Kuala Lumpur, Malaysia. Her current research interests include microfiber for biomedical application.

Hartini Ahmad Rafaie received the B.S. degree in physics and the M.Sc. degree (by research) in advanced materials from the Universiti Teknologi MARA, Shah Alam, Malaysia, in 2007 and 2009, respectively. She is currently pursuing the Ph.D. degree in science with a minor in physics with the University of Malaya, Kuala Lumpur, Malaysia. Her current research interests include oxide materials, composite, nanomaterials, and nanostructures for sensor and photocatalytic applications.

Malathy Batumalay received the B.E. degree in electrical and electronics from University Tun Hussin Onn Malaysia, Parit Raja, Malaysia, in 2004, and the M.Eng. degree in electrical - electronic and communication engineering from the Universiti Teknologi Malaysia, Johor Bahru, Malaysia, in 2010. She is currently pursuing the Ph.D. degree in photonics with the University of Malaya, Kuala Lumpur, Malaysia. Her current research interests include tapered plastic fiber-based optical sensors and coating of sensitive materials.

Sulaiman Wadi Harun received the B.E. degree in electrical and electronics system engineering from the Nagaoka University of Technology, Nagaoka, Japan, in 1996, and the M.Sc. and Ph.D. degrees in photonics from the University of Malaya, Kuala Lumpur, Malaysia, in 2001 and 2004, respectively, where he is currently a Full Professor with the Faculty of Engineering. His research interests include fiber-optic active and passive devices.

Roslan Md Nor received the B.Sc. degree in physics from the University of Malaya, Kuala Lumpur, Malaysia, in 1981, the M.Sc. degree in ionization physics from the University of Wales, Swansea, U.K., in 1985, and the Ph.D. degree from the Queen's University of Belfast, Belfast, U.K., in 1995. He is currently an Associate Professor with the University of Malaya. His current research interests include carbon and oxide nanomaterial, chemical sensors, and radiation dosimetry.

Harith Ahmad received the Ph.D. degree in laser technology from the University of Wales, Swansea, U.K., in 1983. He is currently a Professor with the Department of Physics, University of Malaya, Kuala Lumpur, Malaysia, where he has actively pursued research activities in the field of photonics since 1983. He has authored over 300 professional papers in international journals and conference proceedings. His research interests are in lasers, fiber-based devices for telecommunications, and fiber-based sensor devices. He is a fellow of the Academy of Sciences, Malaysia.