Inline Mach–Zehnder interferometer with ZnO nanowires coating for the measurement of uric acid concentrations

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A simple optical fiber sensor is proposed and demonstrated using a dumbbell shaped inline Mach–Zehnder interferometer (MZI), which is coated with ZnO nanowires for measuring different concentrations of uric acid in de-ionized water. It is found that the interference spectrum of the sensor is red-shifted when the concentration of uric acid rises from 0 to 500 ppm. The peak-wavelength shift linearly increases with the increment in uric acid concentration. The sensitivity of the MZI sensor coated with ZnO is recorded at 0.001 nm/ppm with a good slope of linearity of more than 99% for a limit of detection (LOD) of 5.74%. On the other hand, the sensitivity of MZI-sensor without ZnO coating is 0.0005 nm/ppm with a slope of linearity of more than 99% and an LOD of 8.55%. It can be deduced that the sensitivity of the MZI-coated with ZnO is higher than the one without. This is due to the presence of the ZnO nanowires that trap water molecules within their mesh thereby improving the sensor’s response. These results show that the proposed sensor is applicable and useful for measuring the concentration of biochemical such as uric acid, glucose and fructose.

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1. Introduction

Uric acid is a heterocyclic compound of carbon, nitrogen, oxygen, and hydrogen. It is a product of the metabolic break-down of purine nucleotides. Abnormal level of uric acid in human serum and urine is related to several medical complications, such as gout, Lesh–Nyhan syndrome, and renal failure. A high level of uric acid in serum is also considered as a risk factor for myocardial infarction and stroke [1]. Conventional uric acid biosensors are based on amperometric principle which detects the oxygen consumption, chemiluminescence and fluoride ions [2]. This sensing method is complicated because it requires electrodes to be held at approximately 0.7 V where other biological electroactive molecules react with the surface of the electrodes. Therefore, the need for alternative uric acid biosensors is timely [3–5].

The discovery of ZnO nanostructures in 2001 has generated a great interest in the development of related high performance devices such as nanoelectronics, sensors, field emission and electrodes [6]. ZnO is a unique material that exhibits semiconducting, piezoelectric, and pyroelectric multiple properties. The pyroelectricity of ZnO is attributable to non-centrosymmetrical crystals, and so it has a specific polar axis along the direction of spontaneous polarization [7]. Using a solid–vapor phase thermal sublimation technique, ZnO nanocombs, nanorings, nanohelices/nanosprings, nanobows, nanobelts, nanowires, and nanocages have been synthesized under specific growth conditions. ZnO nanowires grown on the surface of gold coated flexible plastic substrate has been used as a good uric acid biosensor [8]. However, more research on reducing the cost of coating is needed.

Meanwhile, optical fiber has also received much attention for sensing applications. Fiber based sensors have been developed and used for measuring humidity, refractive index (RI), temperature, strain and others [9,10]. Compared to conventional mechanical and electrical sensors, optical fiber sensors offer many advantages such as compactness, high sensitivity, immunity to electromagnetic interference, safety in volatile surrounding and resistance to corrosion. One of the most popular sensor probe made of optical fiber is Mach–Zehnder interferometer (MZI) which is widely used for various sensing purposes [11]. For instance, Wang and Tang demonstrated a refractive index sensor using a photonic crystal fiber (PCF) based interferometer which was realized by fusion splicing a short section of PCF (Blaze Photonics, LMA-10) between two standard
single mode fibers [12]. The fully collapsed air holes of the PCF at the spliced regions allow the coupling of PCF core and cladding modes that realizes a Mach–Zehnder interferometer. But for this PCF, expensive equipment is required for cavity fabrication and thus, the manufacturing cost of the resulting sensor increases.

Recently, Batumalay et al. developed a sensor for detecting uric acid concentrations using a tapered Plastic Optical fiber (POF) coated with ZnO nanostructures by sol–gel immersion technique [13]. The measurement was based on intensity modulation technique where the intensity of the transmitted light was measured for different uric acid concentration in distilled water. However, the intensity based sensor had many limitations that resulted in inaccuracy. In a different work, we demonstrated a simple inline Mach–Zehnder interferometer (MZI) with a dumbbell-shape structure coated with a sensitive material for glucose sensor application [14]. In this paper, we present a new uric acid sensor based on an inline MZI with a dumbbell-shape structure coated with ZnO nanowires as a probe. The MZI is then used to detect changes in uric acid concentrations in distilled water based on wavelength shift instead of intensity. The coating of ZnO nanowires onto the MZI structure is accomplished by a sol–gel immersion method. The proposed MZI structure comprises two bulges connected by a tapered waist. The measurement is based on interferometric technique where the transmission spectrum of the reflected light for different uric acid concentration is examined for sensor with and without ZnO coating. ZnO nanowires is chosen as the coating layer due to its ability to efficiently trap water molecules from the analyte solution. Based on our knowledge, this is the first demonstration of the uric acid sensor using a ZnO nanowire sensing layer in conjunction with interferometric approach. This type of sensor is cheap, robust and more accurate compared to the intensity based approach [13].

2. Experimental arrangement

A microscopic image of the fabricated inline MZI sensor is shown in Fig. 1. In the experiment, a commercial fusion splicer (Sumitomo, Type 39C) was employed to fabricate the bulges on an uncoated standard single mode fiber (SMF). The fiber was cleaved and then fused to form the first bulge. The prefusion and discharge currents were kept at default. The prefusion and fusion times were set at 0.05 s and 1.65 s and a large “overlap” parameter of 80 μm was chosen for fusion splicing. The overlap parameter was the fiber length that was merged by the splicer at the fusion point from both sides to form a bulge. At the fusion point, the fiber ends were heated by arc discharge and fused. An enlarged bulge was formed due to repeated fusion of the softened fiber at the same splicing point. The process was repeated to form the second bulge. By concatenating two such bulges, a dumbbell shaped inline MZI was constructed.

Fig. 1. The microscope image of the fabricated dumbbell shaped MZI. The bulges have center waist diameters of 198 and 196 μm with a tapered waist diameter of 95 μm. As shown in Fig. 1, the distance between the two bulges is about 1000 μm. The dimension of the dumbbell shaped structure is controlled by the fusion splicer program, thus repeatability of its fabrication is not an issue. The operating principle of the proposed sensor is based on the signal interference between core and cladding modes inside the dumbbell structure. The two bulges act as the beam splitter and beam combiner. When the input light beam reaches the first bulge of the sensor probe, it is split into two parts where the first part (core mode) continues to propagate in the core, while the other part (cladding mode) travels in the cladding of the fiber. After the first bulge, the cladding modes travel in the fiber cladding and the surrounding coating layer. Then part of the cladding modes are coupled back to the core mode of the SMF at the second bulge. The inline MZI is formed due to the optical phase difference between the core mode and the higher-order cladding modes.

We chose ZnO nanowires obtained by a sol–gel immersion method as the sensitive sensing material since this nanostructure has its own unique properties [15]. In the experiment, aqueous solution of 0.01 M Zinc Nitrate (Zn(NO₃)₂) and 0.01 M Hexamethylenetetramine (HMTA; C₆H₁₂N₄) were prepared in 100 ml deionized (DI) water. HMTA is highly water soluble and its thermal degradation releases hydroxyl ion which react with Zn²⁺ ions to form ZnO [16]. A typical synthesis of ZnO nanowires in aqueous solution of zinc nitrate and HMTA is based on the following reactions [17].

\[
\text{C}_6\text{H}_2\text{C}_6 + 6\text{H}_2\text{O} \leftrightarrow 6\text{HCHO} + 4\text{H}_3\text{O}^+ \quad (1)
\]

\[
\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \quad (2)
\]
The solution was stirred at 60 °C for 2 h to obtain a clear homogeneous solution and then the solution was kept for 24 h prior to fiber coating process. The deposition process of ZnO nanowire onto the IMZI structure was implemented using a simple manual dip coating technique. In the process, the dumbbell shaped MZI structure was manually dipped into the solution and dried at 60 °C to evaporate the solvent and to remove organic residuals. This dipping and drying procedure was repeated five times to increase the thickness of the coating layer. The dumbbell shaped sensor probe was then characterized using Field Emission Scanning Electron Microscope (FESEM) to investigate the morphology of the ZnO nanowires coating on the tapered waist. Fig. 2(a) and (b) shows the microscope and FESEM images of the sensor probe. As seen in the figure, a high density of ZnO nanowires are visible on the tapered waist of the IMZI. The ZnO nanowires coating is expected to enhance the ability of the probe to sense the surrounding uric acid solution. Fig. 3
shows the cross-sectional SEM image of IMZI ZnO nanowire. The thickness of the ZnO coating layer is measured at around 1.48 μm.

Fig. 4 shows the experimental setup used to detect uric acid concentrations using the inline MZI. The input signal from an amplified spontaneous emission (ASE) laser source is launched into the sensor probe via a 3 dB coupler. The homemade ASE source is obtained from an Erbium-doped fiber amplifier (EDFA) with a wavelength range from 1520 to 1565 nm. The tip of the sensor probe is perpendicularly cleaved to allow 3–4% of the light to be reflected back into the system due to Fresnel reflection. The reflected signal from the sensor is then routed to an optical spectrum analyzer (OSA, ANDO AQ6330) with a resolution of 0.05 nm through the same coupler. In this experiment, the dumbbell shaped MZI probe is immersed in uric acid solution of different concentrations ranging from 0 to 500 ppm. The solution was prepared by mixing uric acid and distilled water with different proportions of 0 ppm, 100 ppm, 200 ppm, 300 ppm, 400 ppm and 500 ppm, which corresponded to mixtures with refractive indices of 1.333, 1.3331, 1.3332, 1.3334, 1.3335 and 1.3336 respectively. Due to the compact structure of the sensor, a single drop of the liquid solution was enough to surround the whole dumbbell shape. The MZI was cleansed with deionized water and compressed air after each measurement.

3. Results and discussion

Fig. 5(a) and (b) shows the reflected spectrum at various uric acid concentrations in DI water, for the probes without and with the ZnO nanowire coating, respectively. It is observed that both probes obtain a comb like reflected spectra. This is attributed to the optical path difference (OPD) between the cladding and core modes, which produces an interference pattern in both dumbbell shaped MZI structures. For both sensors, the interference spectra are red-shifted when the concentration of the uric acid rises from 0 to 500 ppm. Fig. 6 shows the wavelength change of one of the transmission peaks with the increase in uric acid concentration for both sensors. As observed, the peak–wavelength increases linearly as the concentration of the uric acid of the solution rises. The sensitivity of the MZI with ZnO coating is obtained at 0.0005 nm/ppm and the slope shows a good linearity of more than 99.33% for a 5.74% limit of detection (LOD). On the other hand, the sensitivity of MZI-based sensor without ZnO coating is 0.0005 nm/ppm with a slope linearity of more than 99.81% and limit of detection of 8.55%. LOD is calculated by dividing the standard deviation with sensitivity. A system is more efficient when its LOD is lower. Based on these results, it is found that the MZI-coated with ZnO has a higher sensitivity than the one without.

Uric acid is an electrolyte, a substance containing free ions that make it electrically conductive. The free ions attach to the surface of the ZnO nanowires and attract nearby water molecules. The water molecules get trapped within the nanowires mesh due to the electrostatic attraction force from the free ions. As the concentration of the uric acid increases, more free ions are available to attract more water molecules within the mesh thereby increasing the effective refractive index of the surrounding. The change in the refractive index of the surrounding alters the path length difference between the core and cladding modes inside the IMZI, which in turn shifts the interference spectrum to a longer wavelength. The output intensity of the MZI coated with ZnO is governed by:

\[
l = l_1 + l_2 + 2 \sqrt{l_1 l_2} \cos(\phi)
\]  

where \(l\) is the intensity of the interference signal, \(l_1\) and \(l_2\) are the intensity of the light propagating in the fiber core and cladding respectively and \(\phi\) is the phase difference between the core and cladding modes. It is approximately equal to:

\[
\phi = \left( \frac{2\pi |\Delta n_{\text{eff}}| L}{\lambda} \right)
\]  

where \(\Delta n_{\text{eff}}\) is defined as \((n_{\text{eff}} - n_{\text{eff}}^{\text{core}})\) which is the difference of the effective refractive indices of the core and the cladding modes, \(L\) is the length of the interferometer region and \(\lambda\) is the input wavelength.

Reversibility of the results is another important factor in the operation of any sensor system, so this parameter is tested for the reported system. The results of the output measurement as a function of concentration are recorded for two different runs and the results are compared for both MZI-sensors with and without nanowire coatings. As observed in Fig. 7(a) and (b), the maximum difference between the two runs is obtained at about ±0.05 nm and ±0.04 nm for sensors with and without coating respectively. These values are acceptable for a full-scale output of 1550 nm region. These results show that the proposed sensor is applicable and use-

![Fig. 6. The wavelength change of one of the transmission peaks with the increase in uric acid concentration.](image)

![Fig. 7. The reversibility of the results obtained for two different runs for IMZI (a) with ZnO nanowires coating and (b) without nanowires coating.](image)
ful for the measurement of bio-molecular concentration such as uric acid, glucose and sodium chloride. The performance of the uric acid sensor based on dumbbell shaped inline MZI probe is summarized in Table 1.

4. Conclusion

Simple sensors are proposed and demonstrated using a dumbbell shaped inline MZI coated with ZnO nanowires for detecting different concentrations of uric acid in de-ionized water. It is found that the interference spectrum for the sensor is red-shifted when the concentration of uric acid rises from 0 to 500 ppm. The peak-wavelength shift linearly increases as the concentration of the uric acid of the solution increases. The sensitivity for MZI coated with ZnO is obtained at 0.001 nm/% and the slope shows a good linearity of more than 99.33% for a 5.74% LOD. On the other hand, the sensitivity of MZI-based sensor without ZnO coating is 0.0005%/nm with a slope linearity of more than 99.81% and an LOD of 8.55%. It can be concluded that the sensitivity of MZI-coated with ZnO is higher than the one without. This is due to the uric acid being an electrolyte, a substance containing free ions that makes the substance electrically conductive. The MZI coated with ZnO nanowires interact with uric acid due to strong electrostatic interaction and response with increasing concentration. These results show that the proposed sensor is applicable and useful for measuring the concentration of biochemicals such as uric acid, glucose and fructose. The sensor is cheap, easy to fabricate and compact in size.

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References


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