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Fiber Optic based Localized SPR for Nutrients Detection in Modern Agricultural Applications

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Abstract

Detection of nutrients in the hydroponics system, particularly nitrogen, phosphorus, and potassium (NPK) are critical to ensure the good production of crops. Currently, nutrients are analyzed using spectroscopy and electrochemical techniques, which are tedious and sophisticated. This study was conducted to develop a localized surface plasmon resonance (LSPR) fiber optic sensor technique to measure how much content of these nutrients should be added in the soil to increase crop fertility. The main objectives of this study are to study the LSPR fiber sensor technologyon NPK in hydroponic systems, to create a fiber optic sensor technique for measuring NPK in hydroponic systems, and finally to characterize the performance of fiber optic sensors for measuring NPK in hydroponic systems. The utilization of the sensing materials, chitosan in this work is to improve the sensitivity feature of the sensor. Chitosan is coated on the surface of the tapered optical fiber prior to the LSPR NPK detection. The results of the absorption spectra will be visible at the end of the experiment where the obtained data are analyzed using SpectraSuite software. The results show that a good linearity was obtained when used AgNP/chitosan as the sensing material with the sensitivity of 0.041 nm ppm^{-1} in comparison to that of AgNP with the sensitivity of 0.039 nm ppm^{-1}. A better limit of detection (LOD) and limit of quantification (LOQ) was also observed for AgNP/chitosan which are 35.61 ppm and 107.91 ppm, respectively. Meanwhile, AgNP exhibits LOD and LOQ of 106.16 ppm and 494.43 ppm, respectively. It is expected that this work will be a good contributor to the United Nations Sustainable Development Goals (UN SDG), No. 2: Zero Hunger.

1. Introduction

Increasing the yield of plant fertilizers, especially those containing nitrate (N), phosphate (P), and potassium (K) is very important. In China, excessive use of fertilizers has resulted in low efficiency of fertilizer use (35% average) whichcauses low quality of agricultural products and serious environmental pollution [1]. The quantity of NPK depends on the type of plant and growth status while the quantity of fertilizer that needs to be used depends on the current content of NPK nutrients. Next, the use of fertilizers has changed agricultural productivity and its industry has grown significantly since the 1950s [2]. Several factors have helped this growth including microeconomic development, economic globalization technological evolution towards mechanization and automation.

Researchers inagriculture have also been looking for ways to optimize crop yields while minimizing fertilizer use.Integrated cropping system management has been designed to study the spatial perception of NPK [3]. This continuous monitoring along with soil moisture and pH has led to automation in agricultural areas to increase crop productivity. In this context, the development of sensors for nitrogen, phosphorus and potassium (NPK) would be an ideal tool for thesustainability of crop management [4]. However, current knowledge and technology is less sensitive and have not yet beenable to create portable sensors that can measure the three main parameters in either water or soil in a simple, straight-forward, cost-effective way and maintain methodological accuracy.

Optical fibre sensor technology has expanded in many applications with its own advantages such as no electrical circuitry required, free from any electrical disturbance, small size and lightness, speed in transmission and signal reception, large bandwidth, and easy and safe to use [5]. However, the use of ordinary optical fibre for nutrient

monitoring is insensitive due to the thick cladding of the optical fibre, which limits interaction between the contact surface and substrate, leading to low sensitivity. This limitation can be improved by modifying the geometry of the optical fibre to enable the interaction of the optical mode with the surroundings. The evanescent field in the modified optical fibre is exposed beyond the surface of the sensing region; one of such modification methods involves tapering the fibre [6].

The integration of metal thin film and metal nanoparticles with modified optical fibre is to induce a strong plasmonic wave on its surface. Surface plasmon resonance (SPR) and localized surface plasmon resonance (LSPR) are electromagnetic modes formed by collective oscillations of free electrons. The main difference between these two techniques is the structure and shapes of noble metal used. SPR is using metal thin film where the plasmon wave propagates along with the interface between metal thin film and external medium. Meanwhile, for LSPR, metal nanoparticles are used and the plasmon wave is excited on the metal nanoparticle's surface [7]. The performance of the sensor could be further improved by integrating the modified optical fiber with the sensing material. Chitosan, is a type of a bio-based sensing material that possesses remarkable feature in detecting the selected analytes due to the presence of various functional groups in its structure [8].The use of chitosan in this work is expected to improve the sensor performance in terms of sensitivity feature due to the presence of additional active sites provided by such material [8], [9].

In this work, an optical fiber based localized SPR was developed for the NPK detection in aqueous. The developed optical fiber was further integrated with the sensing material, chitosan to improve the sensor performance. The sensor performance was evaluated in terms of sensitivity, linearity, limit of detection (LOD) and limit of quantification (LOQ) features.

2. Materials and Methodology

2.1 Fabrication of the Tapered Optical Fiber

Tapered fibers are produced by slowly stretching optical fibers while they are heated over a flame to soften the glass. This procedure makes the fiber a few millimeters thinner as in Figure 1. The fiber core also becomes thinner by a factor equal to the number of fibers. [10] stated that tapered fibers are also found to be more sensitive than conventional fibers due to the way light propagates in the tapered optical fiber core. A fraction of the optical power is found to propagate outside the tapered optical fiber core. In other words, the evanescent field of the tapered fiber extends beyond the physical boundary of the fiber. Coating the tapered region with a sensing layer enables the interaction of the layer with the evanescent field [6], [11]. The evanescent field will also be affected if the analyte interacts with the sensing layer and changes the properties of the layer [12]. Figure 1 shows the cross-section of the tapered optical fiber.

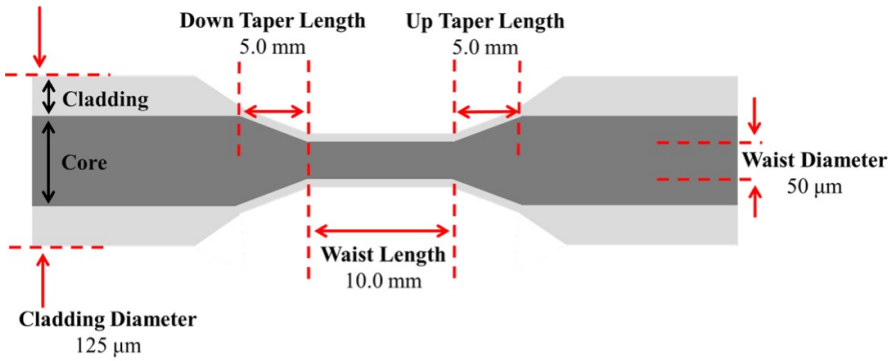

Figure 1. Cross-section of the tapered optical fiber

Prior to sensing performance analysis, the tapered optical fiber is coated with active sensing layers. The active sensing layer is expected to improve the performance of the sensors in terms of sensitivity feature. In this work, 0.5 g of silver (Ag) was used as the first coating layer on the tapered optical fiber surface, followed by the second layer with 0.125 g of Ag. Subsequently, the tapered optical fiber was coated with chitosan, whereas this material is responsible to interact with the NPK analytes.

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2.2 Experimental setup

The coated tapered optical fiber is then connected to the UV-Vis equipment as illustrated in Figure 2. A tungsten-halogen lamp (Ocean Optics HL2000) with a wavelength range of 360-2400 nm was used to transmit light into the optical fiber. A coated tapered fiber was assembled inside the NPK chamber of the holder. A spectrometer (Ocean Optics USB4000) with a spectral range of 400 -1250 nm was used as a light detector to measure the light output intensity of the sensor. The spectrometer is connected to a computer via USB port. Then the spectral data were characterized using SpectraSuite software [13]. Figure 2(a) and (b) show the block diagram and experimental setup for NPK detection, respectively.

2.3 Evaluation of the Sensor Performance

The sensor performance was evaluated based on the sensitivity, linearity, limit of detection (LOD), and limit of quantification (LOQ).

3. Results and Discussions

3.1 Detection of NPK utilizing tapered optical fibre based localized surface plasmon resonance sensor (LSPR)

The interaction between the NPK analyte and the sensor layer was studied by monitoring the reflectance spectrum. The developed sensor was exposed to analytes with different concentrations atroom temperature. The spectral data of the fiber sensor with AgNP is displayed in Figure 3(a). Based on the spectrum graph diagram, the minimum reflection point for each concentration occursbetween 420 nm - 440 nm. The reflection peak trend moves to the right when the fiber is in contact witha higher concentration of phosphorus analyte (20 ppm - 429.37 nm, 40 ppm - 424.22 nm, 60 ppm - 425.27 nm, 80 ppm - 425.01 nm, 100 ppm - 425.01nm). This shows that fibers with AgNP also detect when there is a larger concentration difference. Next, absorption of light by AgNP causes resonance to occur around 400 nm and a deficiency in reflection. The difference in concentration between 40, 60 and 80 ppm are very small. Moreover, fibers coated with AgNP alone are not very sensitive to small changes in concentration.

Meanwhile, Figure 3(b) shows the spectral data of the fiber sensor with AgNP/chitosan where the minimum reflection point for each concentration occurs between 370 - 390 nm. Next, the trend of the reflection peak shifted to the right when the fiber was in contact with a larger concentration of chitosan. This also indicates that the detected light energy decreases. Without chitosan, less light energy is absorbed because the point of minimum reflection occurs in a wider range of wavelengths, making it less sensitive. With chitosan, more light energy can be absorbed because the minimum reflection point occurs in a smaller wavelength range, making it more sensitive.

3.2 Evaluation of the sensor performance

Figure 4 shows the calibration curve for the analyte where the sensor performance is characterized. Sensors are evaluated through three parameters namely range, linearity and sensitivity. The linear range is the concentration range over which the instrument responds linearly. Next, the linearity of the calibration curve can be expressed using the coefficient of determination (R^2). If seen from the graph, the coefficient of determination is 0.936 which is close to the acceptable coefficient value of 0.95. The graph is considered linear because the coefficient value on the graph is close to 0.95. In addition, the slope (m) of the graph is 1.256 where it shows that the sensor produced is ideal because it has great sensitivity and a constant value. The curve has constant sensitivity because it is a linear graph.

Based on the image of the calibration curve data above, the performance of the optical fiber sensor can be measured in two ways, namely sensitivity and linearity. Linearity is a metric that shows how well a curve matches the generated data. The R2 value on the calibration curve indicates the fiber optic linearity of the sensor. The closer the R2 value is to1.00, the more accurate the fiber optic sensor is in measuring absorbance. $R2 \geq 0.99$ is usually considered an excellent sensor value. The data diagram of the calibration curve shows that the R^2 value of the AgNP/chitosan sensor is 0.9264 while the R^2 value of the AgNP sensor is 0.375. The error variability value in AgNP/chitosan optical fiber sensor measurement is 0.0736 and the value for AgNP is 0.625. This shows that the linearity of AgNP/chitosan sensor is better compared to AgNP sensor.

The parameter change required to achieve a standard output change is known as sensor sensitivity. The slope of the calibration curve or the value of m in the equation $y = mx + C$ is another way to determine sensitivity. Next, a sensor with a greater gradient hasa higher sensitivity. Based on the calibration curve data diagram, the equation for the AgNP/chitosan calibration curve is $y = 0.0413x + 6.8457$, according to the equation $y = mx + C$, the sensitivity value, m for the AgNP chitosan optical fiber sensor is 0.0413 while the sensitivity value of the AgNP sensor is 0.0396. In terms of sensitivity, AgNP/chitosan sensors are more sensitive than AgNP sensors. It can be

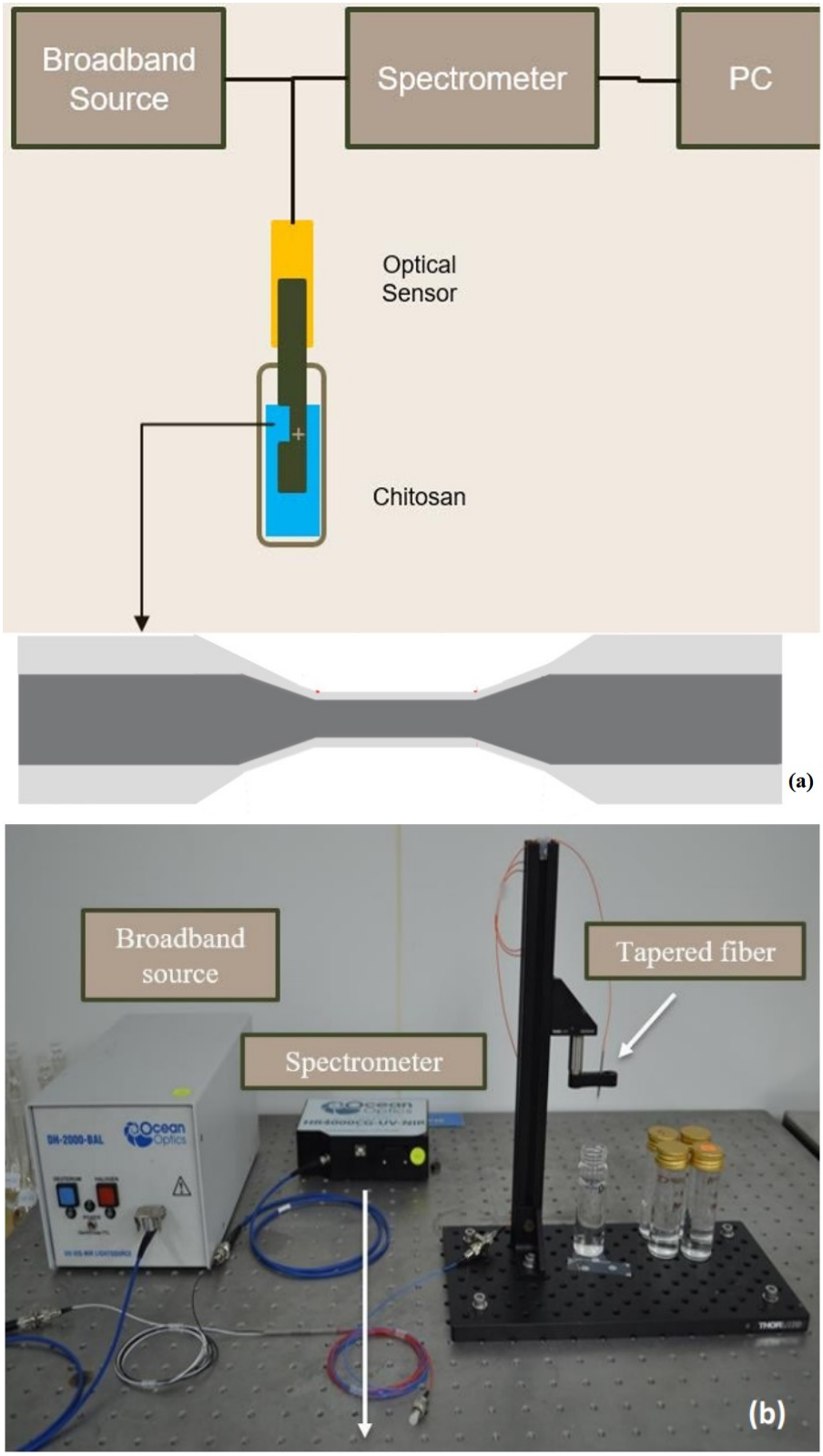

Figure 2. (a) Block Diagram and (b) Experimental Setup

concluded that chitosan can increase the sensitivity of the optical fiber sensor in detecting NPK concentration. Table 1 shows the summary of the LSPR sensor parameters for NPK detection.

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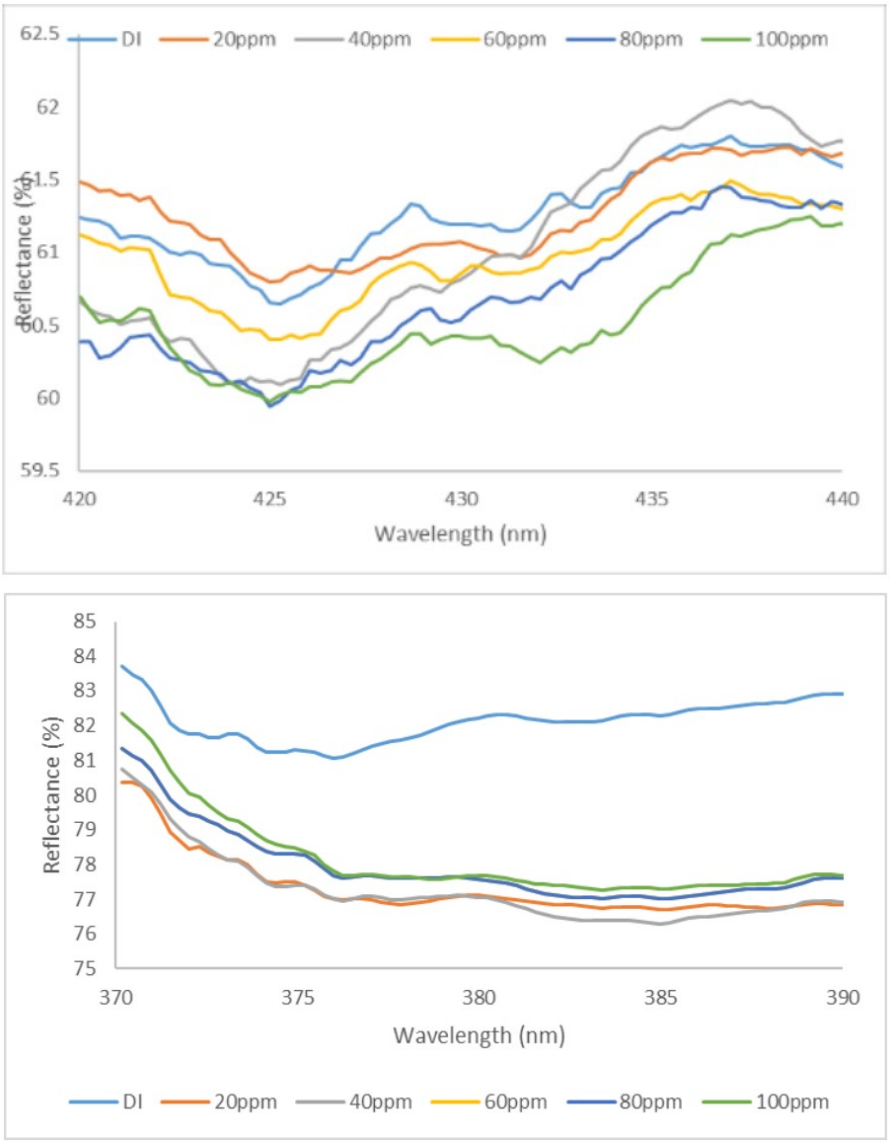

Figure 3. LSPR spectrum for (a) tapered optical fibre coated AgNP, and (b) tapered optical fibre coated with AgNP/Chitosan

The limit of measurement (LOQ) is the lowest analyte concentration that can be measured. The LOQ value of both sensors, AgNP/chitosan and AgNP can be calculated using the formula below:

$$LOQ = 10 \times \frac{\text{Standard error}}{\text{Sensitivity/Coefficient}} \tag{1}$$

Based on Equation 1, the measurement limit value for AgNP/chitosan is 107.91 ppm and for AgNP is 494.43 ppm. This proves that AgNP/chitosan sensors able to detect smaller concentration in contrast to AgNP sensors. The limit of detection (LOD) is the lowest concentration of the analyte in the sample that can be consistently detected with the specified probability. The LOD of AgNP chitosan and AgNP sensors can be calculated using the formula:

$$LOD = 3.3 \times \frac{\text{Standard error}}{\text{Sensitivity/Coefficient}} \tag{2}$$

Based on Equation 2, the detection limit value for AgNP chitosan sensor is 35.61 ppm and for AgNP is106.16 ppm. This shows that the LOD value of the AgNP sensor is greater compared to the Chitosan AgNP value, thus proving that the Chitosan AgNP sensor able to detect small changes in NPK concentration.

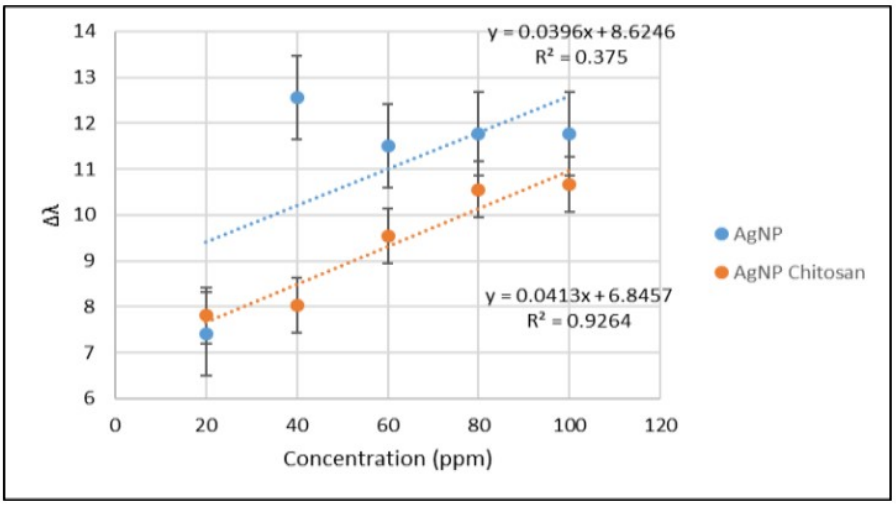

Figure 4. Calibration curve for LSPR NPK sensor

Table 1. Summary of the LSPR sensor parameters for NPK detection

Sensor Parameters	AgNP	AgNP/Chitosan
Sensitivity (nm ppm^{-1})	0.039	0.041
Linearity	0.380	0.930
LOD (ppm)	106.16	35.61
LOQ (ppm)	494.43	107.91

4. Conclusion

This study shows that the application of chitosan as the sensor material able to increase the sensitivity of the LSPR sensor. We can also see that the AgNP/chitosan sensor is more sensitive and has better linearity than the AgNP sensor in detecting the concentration of NPK analytes. A better limit of detection (LOD) and limit of quantification (LOQ) was also observed for AgNP/chitosan which are 35.61 ppm and 107.91 ppm, respectively. Meanwhile, AgNP exhibits LOD and LOQ of 106.16 ppm and 494.43 ppm, respectively. It is expected that this work could be implemented in the agricultural industry to increase the crop production as well as a good contributor to the United Nations Sustainable Development Goals (UN SDG), No. 2: Zero Hunger.

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