Detection of Oleic Acid with Surface Plasmon Resonance Based Optical Fiber Sensor

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ABSTRACT

The oleic acid of vegetable oils provides significant information about the quality and the degree of purity of oil during processing, transportation and storage. By using optical fiber surface plasmon resonance (SPR) based sensor, the detection of oleic acid concentration have been achieved and verified with applying AOCS titration method. The sensing device was a multi-mode optical fiber in which half the core was polished away and a thin-film layer of gold is deposited. The sensor with the high sensitivity of 4800 (nm/RIU) and precise resolution of $1.08 \cdot 10^{-5}$ RIU was obtained. For each 1% increasing in oleic acid concentration, the resonance wavelength shifted by about 5 nm. Since the oleic acid could be accurately calculated as KOH required to neutralize the acid value, the oleic acid traditionally measured by AOCS titration method was applied to verify our experiment results and to correlate the SPR wavelength with the oleic acid concentration. The resonance wavelength shift for increasing oleic acid concentration was consistent with the amount of KOH added.

Keywords: oleic acid, surface plasmon resonance, optical fiber sensor, titration method

以光纖表面電漿共振感測器做油酸檢測

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摘　　要

植物油的油酸提供了關於油品在加工，運輸和儲存期間的質量和純度的重要信息。在本論文中，利用表面電漿共振原理在光纖表面製作出感測器，實現了油酸濃度的檢測，並以 AOCS 滴定法驗證實驗結果。感測器製作是將多模光纖磨掉一半的纖芯，再沉積一層金的薄膜層而成，具有 4800（nm / RIU）的高靈敏度和 $1.08 \cdot 10^{-5}$ RIU 的精確度。每增加 1%的油酸濃度，共振波長移動約 5nm。由於油酸可以準確地以中和酸值所需的氫氧化鉀來計算，所以傳統上都使用 AOCS 滴定法精確測量油酸的濃度，因此我們用滴定法驗證實驗結果，並找出 SPR 波長和油酸濃度的關聯性。結果發現，增加油酸濃度引起的共振波長偏移與加入的氫氧化鉀的量呈線性一致。

關鍵詞：油酸，表面電漿共振，光纖感測器，滴定法

文稿收件日期 106.3.7;文稿修正後接受日期 106.9.19; *通訊作者
Manuscript received March 7, 2017; revised September 19, 2017; * Corresponding author

Ⅰ. INTRODUCTION

During both storage and processing, or using different means of heat or mass transfer, lipids may suffer chemical alterations. It refers to hydrolysis of fats and oils, producing free fatty acids (FFA) by enzymatic action, present in oilseed grains or microbiological origin. Also, hydrolytic rancidity may occur non-enzymatically at high temperatures, producing FFA. It is accelerated by light and heat, the FFA formed being responsible for undesirable flavours and aromas. Acid value, contributed from the oleic acid, measures FFAs and is usually considered to be one of the main parameters to reflect the quality of vegetable oils, degree of refining, as well as the quality change during storage [1, 2]. According to the AOCS (American Oil Chemists' Society) official method, the acidity, which is determined as milligrams of KOH required to neutralize the FFA in 1 g of sample, increases with the deterioration of the oil [3]. However, the AOCS official method is titration analysis, which is time-consuming, labor-intensive, and requires large amounts of organic solvents.

There is a great need for detection of low concentrations or a low number of molecules, especially in food safety inspection and biomedical field. Smaller and more sensitive sensors are required to achieve low detection limits. Since satisfying both the low concentration and absolute number of molecules detected requirement, recently, SPR (surface plasmon resonance) sensors are getting considerable attentions from biomaterials inspection, chemical detection, and physical test etc [4-8]. Two main types of SPR sensor have commonly been employed: prism based [9, 10] and optical fiber based SPR sensor [11, 12]. Normally the former is a rather big device where long turning arms for aligning light sources and detectors were placed. The prism based SPR sensor is not optimal for in situ industrial or environmental process monitoring because of their bulky construction. The recent need of integration and miniaturization has motivated the scientific community to find alternative configurations for SPR devices, in order to have lighter, smaller and more flexible systems. One of the most promising solutions is to use an optic fiber approach. Typically, SPR is excited at the interface between a metal film and a dielectric (sample) medium by means of coupling through a high refractive index (RI) substrate. The fiber core for light transmitting can be used not only as a waveguide but also as a support of the metal film in SPR detection. The optical fields associated with the surface plasmon decay exponentially into both media and thus sense the region near the interface. RI obtained with SPR can be used to measure acid value of vegetable oils by sensing the change in the amount of FFA [13]. The objectives of this study, therefore, are to develop a SPR based optical fiber sensor to measure oleic acid and to correlate the results with those of the AOCS official titration method [3].

Ⅱ. EXPERIMENT

2.1 Sample Preparation

In general, oleic acid is only tiny volume contained in vegetable oil so it is difficult to clarify the variation of RI of vegetable oil. In this experiment, oleic acid was dissolved in ethanol to obtain the concentration from 0 to 6% v/v in steps of 1% as sample solution. The refractometer (R-5000, ATAGO Co. Ltd.) was applied for RI measurement of sample solution of oleic acid because of the ease and speed with which it can be determined precisely and the small quantity of sample needed.

2.2 Sensor Fabrication

In order to enhance the sensitivity, the guiding properties of the fiber have to be weakened. The side polishing method offers a simple implementation since the mechanical resistance of silica fiber allows an easy removal of a portion of the cladding and core. In addition, side polished optical fiber sensors have demonstrated the advantages of an immediate response, high recurrence, low insertion loss, mechanical stability, and simple fabrication process. The schematic structure of optical fiber SPR sensor is shown in Fig. 1. The graded-index multimode optical fiber with a 62.5 μm core diameter and a 125 μm cladding diameter

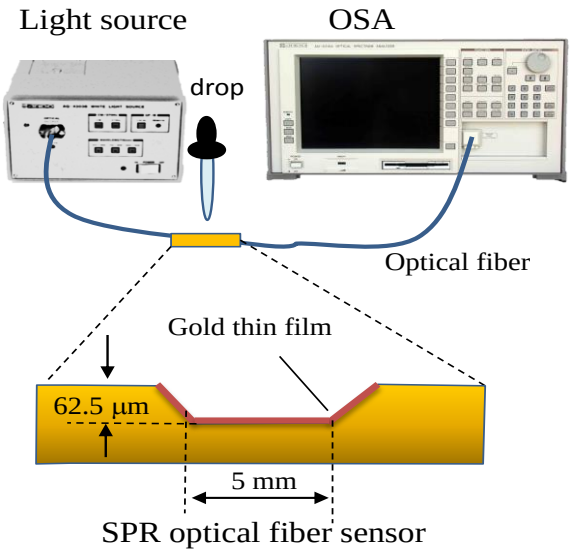
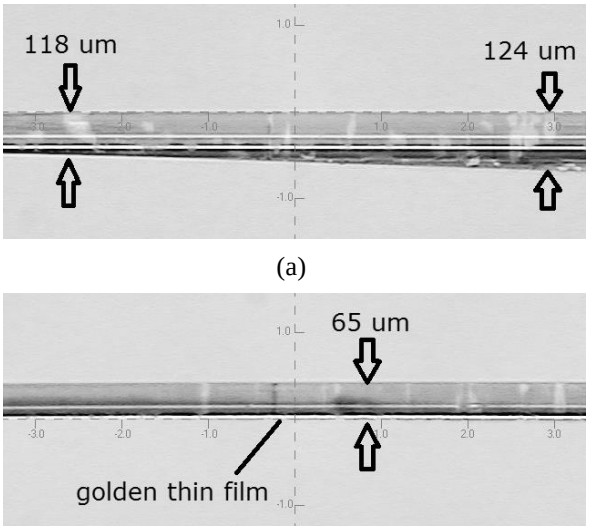


Fig. 1. The schematic structure of optical fiber SPR sensor and the sensing system.

purchased from Prime Optical Fiber Corporation (POFC) was side-polished to make an optical fiber sensor. For high yield rate processes, a silicon V-groove must be fabricated to hold bare fibers. The V-groove channel was 5 mm in length and 125 μm in width, respectively. The optical fiber was mounted on the V-groove holder with photoresist and monitored by optical microscopy. Afterwards, lapping plate and three kinds of abrasive paper with various degree of roughness 6 μm, 1 μm and 0.1 μm were used to polish side of the fiber in turn. In order to increase the sensitivity of the SPR measurements, the dimensions of the polished surface, length and depth were 5 mm and 62.5 μm. In our previous work , three kinds of SPR sensors with different side-polished lengths of sensing area of 5, 10, and 15 mm had been measured and the result shows that three kinds of the side-polished lengths is approximated to the same performance [14]. It indicates the polished length of the sensing fiber with 5 mm is long enough to deplete TM modes guided on a side-polished fiber sensor, and to increase the side-polished length cannot enhance the SPR response. Moreover, increasing the length of a polished surface not only weakens the SPR response, but also decreases the transmitted light. Then, the processed optical fiber was ready for metallic film coating. The gold thin film was deposited on the polished surface by a DC sputtering system (ULVAC Co., Japan). The thickness of the gold thin film was about 50 nm, and it was observed by SEM (scanning electron microscope, JEOL 7000, JEOL). The photograph of a side-polished optical fiber of partial taper structure and the sensing region are shown in Fig. 2. The length of taper and sensing region are 1.5 mm and 5 mm, respectively.



(a)

(b)

Fig. 2. The photo of a side-polished optical fiber (a) the taper structure (b) the sensing region

2.3 SPR Measurement

A schematic giving the details of experimental set-up is shown in Fig. 1. The halogen white light (Ando Electric Co.,Ltd. AQ4303B) covers the band of 400 – 1800 nm work as input source and the optical spectrum analyzer (Ando Electric Co.,Ltd. AQ6315B) as detector to measure the spectrum of sensors for different RI. First, we recorded the spectrum without any liquid but the air surrounding the sensing region as referenced spectrum. Then, we introduced drops of samples without disturbing optical fiber sensor and measured the spectrum, respectively. The air spectrum was used as a reference to normalize the transmittance of SPR optical fiber sensor spectra taken from the sample solutions. Since there was no SPR excitation for air of RI 1.0, this normalization provided an effective means to measure SPR spectrum.

2.4 AOCS Titration Method

Acid values of samples were determined using AOCS titration method. 10 drops of phenolphthalein indicator were added dropwise to all the oleic acid sample solution. Titrations were performed using accurately standardized 5.6 g/L potassium hydroxide dissolved in ethanol to the end point of definite pink color which persisted at least for 30 s. AV was expressed as mg KOH/g sample.

Ⅲ. RESULTS AND DISCUSSIONS

3.1 RI of Oleic Acid

Fig. 3 shows the correlation between RI of oleic acid sample solution of concentration from 1% to 6% determined with refractometer. A good linear fitting between the RI and the concentration oleic acid of experimental results can be observed, which shows the RI will increase 0.001 as the oleic acid concentration increased by 1%. The measured RI of sample solution is also the same as the calculated results according to the concentration where RI of ethanol and oleic acid is known as 1.360 and 1.458, respectively. The RI of fats and oils is recognized relating to their average degree of unsaturation, and could be used to observe the progress of reactions such as hydrogenation and isomerization.

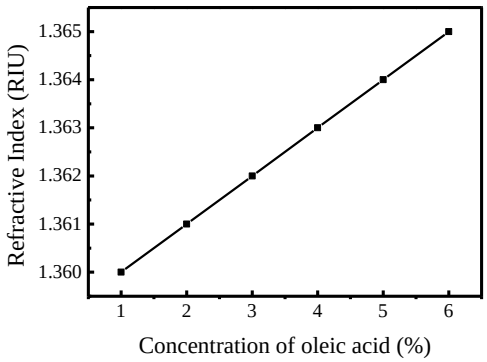


Fig. 3 RI of oleic acid sample solution determined with refractometer.

3.2 SPR Spectrum

Fig. 4 shows the SPR transmittance spectra normalized to the air spectrum for oleic acid sample solution. It can be noted that there is a dip at a particular wavelength in each curve known as the resonance wavelength. The

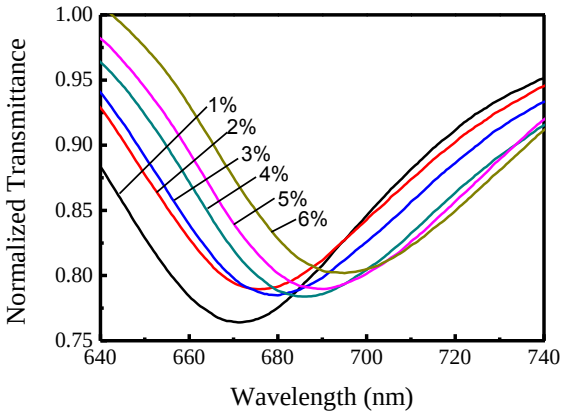


Fig. 4 The SPR spectra due to concentration of sample solution from 1% to 6% in steps of 1%.

resonance wavelength is 671.4 nm for 1% sample concentration and shifts to 695.0 nm for 6%. As the higher the oleic acid concentration, the longer resonance wavelength will be. In terms of calculation, for each 1% increasing in oleic acid concentration, the SPR dip shifts by about 5 nm.

Resolution (R_n) is one of the most important parameters for a sensor and can be defined as the smallest change it can detect in the quantity that it is measuring. In other words, it is the minimum quantity we can measure with the sensor. We calculate the resolution of the RI sensor by Eq. (1)

$$R_n = \frac{\delta \mathrm{n}}{N_{tot}} = \frac{\delta n}{\delta \lambda_{res} \cdot N_{nm}} \qquad (1)$$

where δn is the RI difference of two sample solutions and N_{tot} is the total measuring points we obtained from the OSA, which were connected with the sensor. N_{tot} can be calculated by $\delta\lambda_{res}$, resonance wavelength difference between the two samples, and N_{nm}, the sampling points per nanometer, which depends on the resolution of OSA. No significant change was observed in the RI of the samples with refractometer. SPR sensor is capable of detecting small changes of the surrounding medium in real time. That is, by detecting small RI variation, a SPR sensor could quantitatively describe the interaction between oleic acid and sensing area of gold film. In this study, we could reach approximately $1.08 \cdot 10^{-5}$ RIU compared to $1 \cdot 10^{-3}$

RIU in using conventional refractometer. The sensitivity of SPR sensors is up to about 100 times larger than refractometer.

The sensitivity (S_n), another critical parameter of an SPR sensor, in an optical fiber based configuration is defined as the shift in resonance wavelength per unit change in the RI. If the shift is large, sensitivity is high. As shown in Fig. 4, if the RI of the sensing layer is altered by δn, the resonance wavelength shifts by $\delta\lambda_{res}$. The sensitivity of an SPR sensor with spectral interrogation is defined as

$$S_n = \frac{\delta\lambda_{res}}{\delta n} \qquad (2)$$

To calculate the sensitivity, SPR wavelength is plotted as a function of RI. The slope of this straight line gives the sensitivity of the sensor and the value of 4800 (nm/RIU) is achieved in this experiment. With the high sensitivity and precise resolution, this optical fiber sensor could be also used to determine the RI according to SPR wavelength.

3.3 AOCS Titration

Traditionally, the acid value could be measured by AOCS titration method precisely. Here we use titration to verify our experiment results and to correlate the SPR wavelength and the oleic acid concentration. The concentration of oleic acid is proportional to the amount of potassium hydroxide added, and the more the oleic acid is added, the more the strong base (KOH) is needed. SPR wavelength and acid value of sample solution according to the concentration of oleic acid was plot in Fig. 5. The oleic acid concentration being increased by 1%, the consumption of KOH is about 27 mg. The resonance wavelength shift for increasing oleic acid concentration was consistent with the amount of KOH added. Comparison of the two linear fitting lines, the AOCS titration experimental result shows good agreement with that of optical fiber SPR based sensor.

Ⅳ. CONCLUSIONS

By using optical fiber SPR based sensor and applying AOCS titration method, the detection of oleic acid have been achieved. The correlation between oleic acid concentration and SPR wavelength is also performed. For each 1% increasing in oleic acid concentration, the SPR wavelength shifts by about 5 nm. Based on the measured SPR resonance wavelength, the optical fiber sensor with the high sensitivity of 4800 (nm/RIU) and precise resolution of $1.08 \cdot 10^{-5}$ RIU, which approximately is up to about 100 times larger than conventional refractometer, is obtained. In addition, the oleic acid traditionally measured by AOCS titration method is applied to verify our experiment results and to correlate the SPR wavelength and the oleic acid concentration. The oleic acid concentration being increased by 1%, the consumption of KOH is about 27 mg. The resonance wavelength shift for increasing oleic acid concentration was consistent with the amount of KOH added.

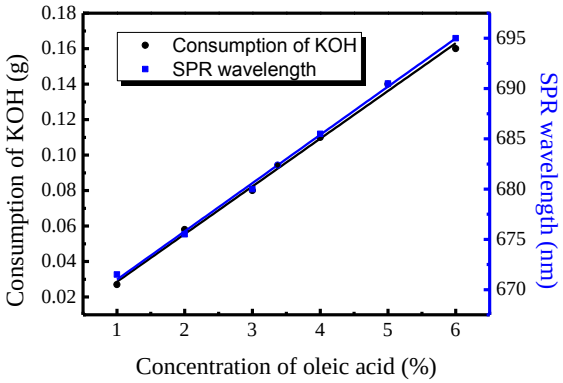


Fig. 5. Correlation between SPR wavelength and consumption of KOH for different concentration of oleic acid. %

Furthermore, the optical fiber SPR based sensor has some merits such as small size, low cost and suitability for in vivo testing. The sensor has the ability to be applied for chemical and food safety sensing.

ACKNOWLEDGEMENTS

The authors would like to thank the Ministry of Science and Technology for financial support under the contracts MOST 106-2221-E-130-011. The authors are grateful to Mr. Li Bing-Ru and Mr. Wang Chun for optical fiber sensor fabrication and SPR measurement. The authors also thank Graduate Institute of Electro-optical Engineering, Tatung University

for supplying optical fiber polishing machine and sputtering equipment.

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