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Localized Surface Plasmon Resonance Refractometer Based on No-core fiber

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ABSTRACT

A novel optical fiber refractometer based on localized surface plasmon resonance (LSPR) is presented. The sensor was prepared by splicing a short segment of no-core fiber (NCF) between two multimode fibers. A gold nanoparticles (AuNPs) film was self-assembled on the sidewall of the NCF. When LSPR peak wavelength is used to investigate the refractive index (RI), sensitivity of 121.88 nm/RIU ($R^2 = 0.9107$), 523.14 nm/RIU ($R^2 = 0.983$) with limit of detection 1.64×10^{-3} RIU, 3.82×10^{-4} RIU over the RI range of 1.33-1.37 and 1.37-1.42, respectively. When normalized transmittance is used to investigate the performance of the sensor, sensitivity of -279 %/RIU ($R^2 = 0.9922$) with limit of detection 4.61×10^{-5} RIU over the RI range of 1.33 -1.42.

Keywords: localized surface plasmon resonance (LSPR), gold nanoparticles, optical fiber sensor, self-assembly

1. INTRODUCTION

Localized surface plasmon resonance (LSPR) is very popular in molecular detection as the electromagnetic field near the nanoparticles surfaces is very sensitive to refractive index change [1, 2]. Compared to the similarly Surface Plasmon Resonance (SPR) [3] technic, LSPR sensor besides has the advantages of SPR sensors, such as the high sensitivity, label-free and real time detection, also offers flexibility in design as the LSPR peak wavelength and its width can be controlled via the composition, size, shape of the metallic nanoparticles [4,5].

Several optical fiber sensors based on LSPR for biochemical sensing have been reported [6-10]. In most of these works, fiber cladding is removed to extend the evanescent field to the outer fiber to excite LSPR. This method always involves chemical etching which is very dangerous and could also weaken the sensor. The no-core fiber (NCF) is a high-precision pure silica fiber and has been utilized in refractive index [11] and humidity [12] monitoring. In this paper, a new structure refractometer that use NCF for exciting LSPR is proposed, offering easy fabrication and high sensitivity.

2. EXPERIMENT

2.1 Preparation of the fiber.

A 20 mm section of NCF (Prime Optical Fiber Corporation) was simple spliced between two multimode fibers (MMF) (Corning, 62.5/125). The schematic diagram of the proposed sensor is shown in Fig. 1.

2.2 Preparation of AuNPs.

Spherical AuNPs of 10 nm radius were synthesized using Turkevitch's method [13]. 100 ml of 1 mM aqueous chlorauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, Acros) was heated to boiling under constant vigorous stirring. 10 ml of 38.8 mM sodium tricitrate (trisodium salt 98%, Acros) was rapidly added. When the colour of the mixture solution turned to red or purple, a further

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10 mins boiling continued. Then the mixture solution was continuously stirred till it cooled down to the room temperature.

2.3 Coating AuNPs onto fiber

The self-assembly method was utilized to prepare AuNPs film on the fiber surface. Firstly, the sensitive section of the sensor was immersed in Piranha solution (H_2SO_4 (95%–97%, Merck) and H_2O_2 (30%, Merck) in 7:3 volume ratio) for 1h for hydroxylation. The optical fiber was then rinsed by distilled water and dried under N_2 . Secondly, the piranha-treated fiber was immersed in 5% (v/v) 3-aminopropyl trimethoxysilane (APTMS, 97%, Aldrich) methanol (Merck) solution for 4 hours for silanization. The amination-functionalized fiber was rinsed by methanol and then placed in an oven at 120 °C for half an hour to activate the silanization process. Finally, the fiber was immersed in AuNPs solution for 6 mins to enable the AuNPs immobilize onto the fiber surface. The LSPR spectra of the assembly process were monitored. Fig.2 shows the schematic diagram of AuNPs assembly on NCF.

Fig. 1 Schematic diagram of the proposed sensor. Fig. 2 Schematic of self-assembly of AuNPs on the NCF surface by chemical modification with APTMS.

2.4 Experimental setup

The experimental setup for evaluating the performance of the proposed LSPR sensor is shown in Fig.3. The AuNPs coated sensor was connected between a white light source (AQ4305, Yokogawa) and a mini-spectrometer (USB4000, Ocean Optics). Two fiber holders were used to hold the sensor straight in a sample solution to prevent fluctuations. The spectra displayed by a computer which connected to the mini-spectrometer and running the SpectraSuite Software.

Fig.3 Schematic of the experimental setup.

3. RESULTS AND DISCUSSION

Fig.4(a) shows the absorbance spectrum of the synthesized AuNPs colloid which was measured by a UV-Vis spectrometer (UV-2450, Shimadzu). The transmission spectrum of the AuNPs uncoated fiber was collected as reference, I_{ref} , in the calculation of the absorbance ($-\log_{10}(I/I_{\text{ref}})$) of the sensor. A series of absorbance spectra during the assembly process were recorded (Fig. 4(b)). A long wavelength shift and an increase in absorbance peak were observed. This illustrates that the quantity of AuNPs immobilized on the optical fiber has increased and the interparticle spacing between AuNPs is reduced. Fig.4(c) shows the trends of the absorbance peak intensities as a function of AuNPs assembly time. An initial rapid assembly process was observed due to a great number of spots for AuNPs absorption. Then the increase in peak intensities plateaued due to the reduction in available spots and interparticle electrostatic repulsion between AuNPs.

The sensitivity of this proposed sensor was evaluated by immersing the sensitive section in sample solutions with different refractive indices. The absorbance spectra at different refractive indices are shown in Fig. 5(a). As observed from

Fig.4. (a) Absorbance spectrum of AuNPs colloid. (b) The absorbance spectra of AuNPs films at different assembly time. (c) the trends of the absorbance peak intensity as a function of assembly time.

Fig. 5(a), the absorbance peak shifts towards longer wavelengths as the refractive index is increased. Fig. 5(b) shows the absorbance peak position for different refractive indices. In order to determine the sensitivity, the response of the sensor is divided into 2 quasi linear regions and fitted (Fig. 5(c)): first region of 1.33-1.37 with a sensitivity of 121.88 nm/RIU, second region of 1.37-1.42 with a sensitivity of 523.14 nm/RIU. The limit of detection (LOD) is 1.64×10^{-3} RIU and 3.82×10^{-4} RIU respectively by considering that the spectral resolution of the spectrometer is 0.2 nm.

Fig.5 (a) Fig.6 Absorbance spectral at different refractive indices. (b) Absorbance peak position for different external RI and (c) RI Sensitivity of the sensor.

Fig. 6 (a) The transmittance spectra of the sensor in solutions of different refractive index. (b) The transmittance at 540.02 nm as a function of the refractive index

The performance of the proposed sensor to RI was also characterized using the transmittance change, at a specific wavelength. The transmittance spectrum is plotted in Fig.6a. Fig. 6b shows the relationship of the transmittance versus RI at wavelength, $\lambda = 540.02$ nm (marked by a vertical line in Fig.6a) before and after AuNPs coating. A much steeper decrease in transmittance can be seen from AuNPs coated fibers due to the evanescent field absorption of immobilized

AuNPs on the fiber surface. Sensitivity is -279 %/RIU with $R^2 = 0.9922$. The limit of detection (LOD) which calculated from σ/S is determined to be 4.61×10^{-5} RIU.

4. CONCLUSION

An optical fiber refractometer utilized self-assembly method to immobilize AuNPs has been demonstrated. Two methods have been used for characterizing the performance of the proposed sensor to external refractive indices. The normalized transmittance of the LSPR sensor exhibits good linearity ($R^2 = 0.9922$) with sensitivity of -279 %/RIU in the region 1.33 -1.42, with a limit of detection of 4.61×10^{-5} RIU. The proposed sensor fabricated using simple splicing and chemical surface modification is a low-cost sensor.

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