



Dual Kretschmann and Otto configuration fiber surface plasmon resonance biosensor

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Abstract: We present a dual-resonance fiber surface plasmon resonance (SPR) sensor for biological analysis. The sensing element was fabricated by sequentially sputtering layers of indium tin oxide (ITO) (100 nm thickness) and Au (35 nm thickness) on the surface of an optical fiber. The refractive index dispersion effect of ITO material led to resonances in the near infrared and visible wavelength regions. The refractive index of ITO is larger than the optical fiber in visible spectral area (400 to 733nm), such that the structure is a typical Kretschmann configuration surface plasmon resonance sensor. However, an Otto configuration is observed in the near infrared area (NIR) due to the ITO refractive index being smaller than the fiber core. We characterized the sensor performance by measuring bulk refractive index (RI) sensitivity in the two configurations, which were 1345 nm/RIU in the Kretschmann configuration and 1100 nm/RIU in the Otto configuration. In addition, this sensor was applied for real-time and label-free monitoring of the IgG/anti-IgG biomolecular interaction. As a robust and ultra-compact SPR sensor, which possesses wide detection range and is highly sensitive, this fiber SPR sensor can be applied for real-time biological analysis and monitoring.

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1. Introduction

SPR is a phenomenon occurring from the coherent charge density oscillation at a metal-dielectric interface when the wave vector of the incident light is equal to that of the surface plasmon (SP) wave supported by the interface. Due to its highly enhanced local electromagnetic field sensitive to the surrounding medium, SPR sensing has been highly popular for designing high-sensitivity sensors [1,2]. Many SPR-based sensors have been reported in the field of environmental monitoring, food safety, medical diagnosis and biomolecular interaction analysis [3–8]. Compared to prism-based SPR sensors, fiber optic SPR sensors are more suitable for *in situ* analyses and are more conducive to miniaturization [9–12].

Conducting metal oxides and other new materials are increasingly used for SPR sensors [13–16]. Owing to its characteristics of high transmissivity of visible light, low electrical resistivity and wide band gap semiconductor, ITO has been widely used as transparent conductor. Additionally, compared with gold and silver, there is no involvement of interband transition and agglomeration problems in ITO films [17]. The detectable spectral range of most metal-based optic fiber SPR sensors is narrow in the visible spectrum [18–20], which seriously restricted the sensing application and effective measurement range of SPR sensors. Some multiple spectrum methods have been proposed based on sensor configuration and mode of detection to overcome the above problem [21,22].

In this paper, we investigate the sensing performance of a fiber optic SPR sensor with a double layer structure of 35 nm Au and 100 nm ITO, which develops a new approach to obtain a dual plasmon resonance in the visible and in the NIR region. Strong material dispersion of ITO film sandwiched between Au film and fiber leads to the presence of two plasmon resonances. Theoretical analysis confirmed that the dip in visible range was induced the excitation of the SPR in the Kretschmann configuration and the dip in the near-infrared

range is generated by SPR in the Otto configuration. The above two different ways of SPR excitation is simultaneously demonstrated in single structure design, which is attributed to strong index dispersion of ITO film. However, the experimental results show that the two resonances are both sensitive to RI of ambient environment, and the resonance wavelengths of two dips shifts towards the longer wavelength as the RI increases. Furthermore, real-time and label-free monitoring of IgG/anti-IgG biomolecular interaction is also implemented to confirm the biosensing potential of this SPR sensor prototype.

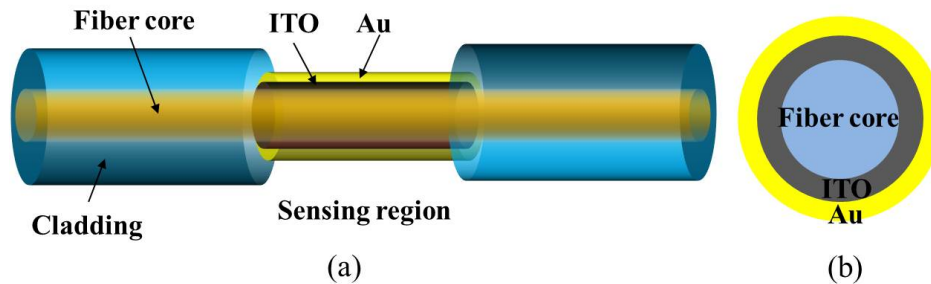


Fig. 1. Optic fiber sensor probe consists of an ITO/Au two-layer structure. (a) Schematic diagram and (b) cross section of the sensing probe.

2. Structure and theoretical analysis

Figure 1(a) shows the schematic diagram of the fiber optic sensor probe consisting of an ITO/Au double-layer structure. The cross section of the sensing probe is also depicted in Fig. 1(b). A 6 cm length multimode plastic cladding silica fiber with 400 μm core diameter and 0.37 numerical aperture was used to fabricate the sensing probe. A 100 nm ITO and a 35 nm Au layer were successively deposited on the 5 mm unclad fiber core to form the sensing region. Before sputtering, the unclad fiber was cleaned with deionized water and acetone, and dried with a pure N_2 gas stream. The ITO and Au layers were sputtered by using the Turbo Sputter Coater (K575XD from E.M. Technologies Ltd. Ashford, Kent).

The simulated transmission spectra were obtained by using the transfer matrix method [23]. In the simulation, the designed principle of fiber sensor was considered as a four layers structure including glass layer, ITO layer, Au layer and sensing medium. The core of optical fiber with a RI of 1.457 was set as the first layer or prism layer. ITO layer and Au layers were the second and the third layer, respectively. The dielectric constant of Au layer was expressed by Drude-Lorentz model in ref. 24 and the dielectric constant of ITO comes from ref. 23. The last layer of the sensing region is the sensing medium.

The simulations based on the FDTD algorithm were performed to obtain magnetic field distribution. The Bloch boundary conditions were applied in x direction and perfectly matched layers are used in y direction. The grid size in the x and y directions was $1 \times 1 \text{ nm}$, respectively, in order to satisfy the integer number of grid in simulation region.

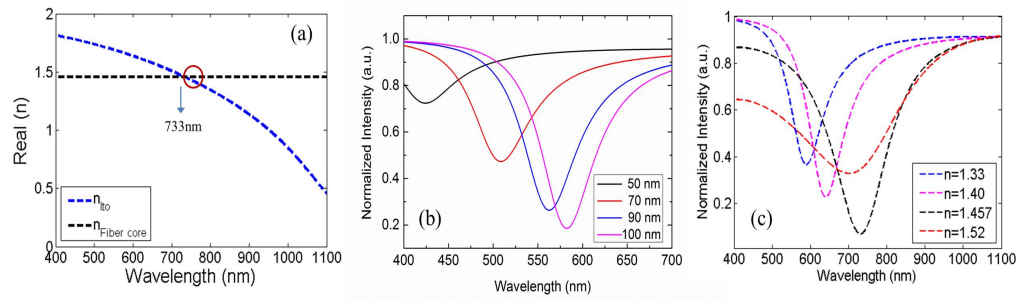


Fig. 2. (a) The dispersion curve of ITO material; (b) Normalized spectra response for the same sensor probe with different thickness of ITO coatings; (c) RI response of ITO coating with 100nm.

In order to investigate the role of the ITO layer in the ITO/Au double-layer structure, we analyzed the dispersion effect of refractive index of monolayer ITO by using the above mentioned transfer matrix method and FDTD method. Figure 2(a) shows the relationship between refractive index of fiber core and ITO material. It can be seen clearly that ITO layer has strong index dispersion. When the wavelength is less than 733nm, the refractive index of fiber core is less than that of ITO material; however, when the wavelength excess 733nm, the situation is the opposite. As illustrated in Fig. 2(b), we studied the normalized spectral responses of the sensor probes with different thicknesses of ITO. There was always a reflection dip in the visible spectrum as the thickness of ITO layer ranged from 50 to 100 nm. According to the excitation condition of SPR, SP wave cannot be excited at the ITO/air, which led to the interrogation on the origin of the reflection dip in the spectrum. To better understand this, we present the refractive index response of 100 nm ITO coating in Fig. 2(c). When the RI of ambient environment was 1.457, consistent with that of fiber core, the reflection minimum was observed at the wavelength of 732 nm. Under these conditions, the three layer structure can be treated as one material with the same refractive index 1.457. All incident light transmission and the reflection reach the minimum value. However, the refractive index of optical fiber core and ITO material is not equal in other conditions, which led to the reflection at interfaces. The reflection properties were in direct relationship with the difference between the refractive index of optical fiber core and ITO material. According to the above analysis, we concluded that the reflected minimum is the result of ITO material dispersion.

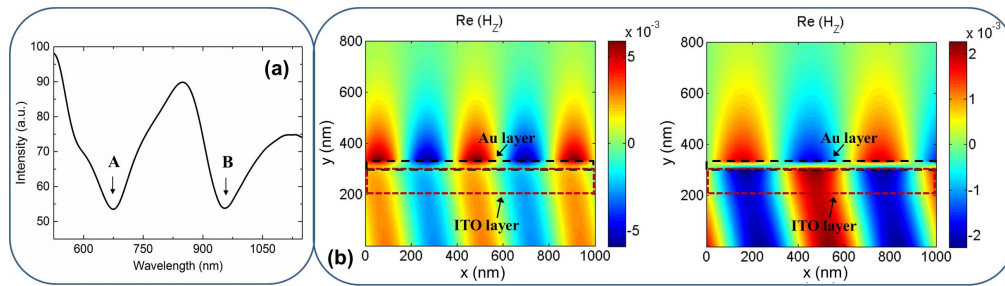


Fig. 3. (a) Experiment transmission spectrum of fiber SPR sensor; (b) Real part of spatial magnetic field in z direction at the reflection minimum value for two dips.

Figure 3(a) shows experiment transmission spectrum of the sensor with 100 nm ITO film coated with 35 nm Au film, with these thicknesses we can get ideal spectrum. There are two evident resonances labelled A and B in the transmission spectrum. In order to explore the generation mechanism of the two resonances, we analyzed the real part of spatial magnetic field in z direction at the reflection minimum value for two resonances. As shown in Fig.

3(b), the black and red dotted lines represent the boundary of gold layer and the ITO layer, respectively. The left-hand side of Fig. 3(b) shows the real part of spatial magnetic field in the z direction at the reflection minimum value for resonance A. It is obvious that the magnetic field was mostly confined on the surface of gold layer with the characteristic of SPP. The refractive index of fiber core was less than that of ITO material for wavelengths less than 733nm, typical of the Kretschmann configuration. Therefore, the resonant dip in this wavelength range is associated to the SPR phenomenon in this configuration.

The right-hand side of Fig. 3(b) shows the real part of spatial magnetic field in z direction when the wavelength exceeds 733nm at the reflection minimum value for resonance B. Notable differences are seen from the previous case. In this case, the refractive index of ITO material is less than that of fiber core. The refractive index distribution and the light path is typical Otto structure. The attenuated total reflection occurs at the interface of the bottom surface of Au film and ITO layer. Because of the thin gold layer, the surface plasmon modes at the surface of gold and outer medium layer are also dictated by mode coupling. Under these conditions, the electromagnetic field distribution of the surface plasmon modes at the two surfaces was the opposite of the Kretschmann configuration, which resulted in the antisymmetric mode of metal waveguide layer. As shown in Fig. 3(b), comparing to resonance A, the field enhancement of the surface plasmon mode at the interface of gold layer and outer medium layer for resonance B is weaker, which lead to the smaller bulk refractive index sensitivity. The result is consistent with the experimental data in Fig. 4.

3. Experiment and discussion

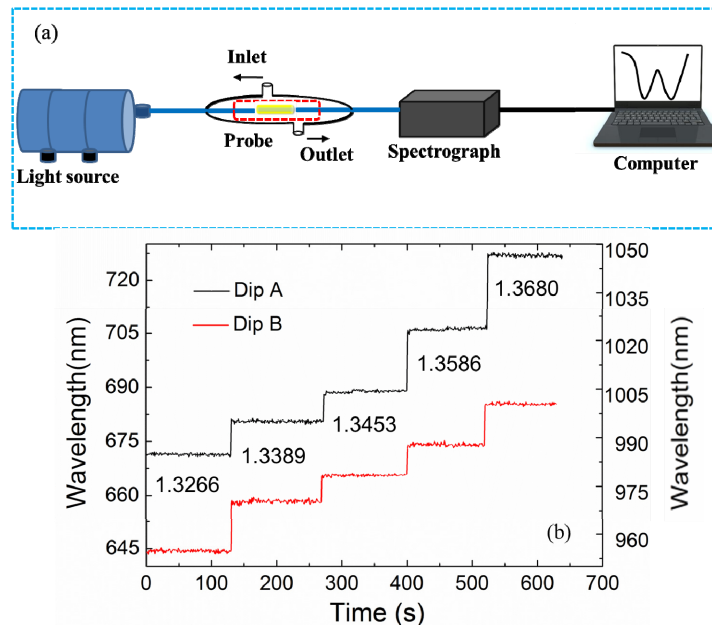


Fig. 4. (a) Experimental setup of the dual dips optical fiber sensor system; (b) RI response of two resonances.

Figure 4(a) shows the experimental setup of the Otto-Kretschmann fiber-optic SPR biosensor. Light from a halogen lamp (HL-2000, Ocean Optics, Inc.) was launched into the one end of the probe. The transmission spectrum was collected at the other end of the probe through a spectrometer (iHR550, Horiba, Inc.) and was displayed on a computer. Moreover, the two end faces of fiber were polished with emery papers to reduce the light loss. The experimental

samples were injected into the flow cell by a peristaltic pump at a controlled flow rate (1.0 mL/min).

We then analyzed RI sensitivity of the sensor to quantitatively evaluate the sensing performance of the Otto-Kretschmann fiber-optic SPR sensor. RI sensitivity, S , is defined as the resonance wavelength shift, $\Delta\lambda$, for a change in the bulk RI, Δn (*i.e.*, $S = \Delta\lambda/\Delta n$). Sodium chloride solutions with different concentration were prepared as the RI samples, and the corresponding RI range was from 1.3266 to 1.3680. The responses of two resonances to different surrounding RIs are shown in Fig. 4(b). As the surrounding RI increases, the wavelengths of two resonances showed red shifts, and increased linearly as the RI increased from 1.3266 to 1.3680. From the linear fit, the RI sensitivities are 1345 nm/RIU and 1100 nm/RIU for Kretschmann resonance and Otto resonance, respectively. The laboratory was maintained at 25°C during the test.

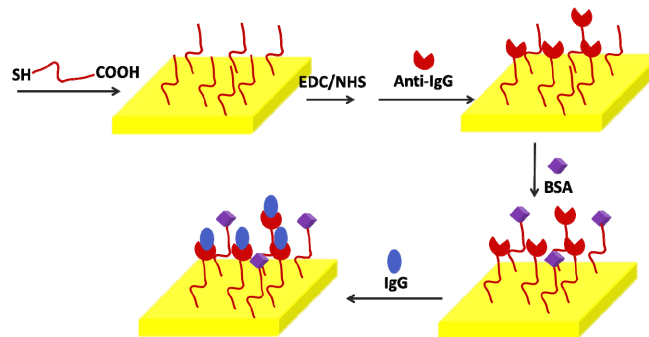


Fig. 5. Antibody immobilization procedure on the surface of the sensing probe.

After experimental demonstration of the RI sensing of the probe, we used the same procedure to investigate the biomolecule sensing capability of the proposed SPR sensor. We carried out model experiments in a buffer solution to kinetically monitor the molecular recognition events. Anti-rabbit immunoglobulin G (IgG) was functionalized on the surface of sensing region, as the molecular recognition probe to specific binding with IgG. The immobilizing process of IgG is depicted in Fig. 5. The sensor probe was ultrasonically cleaned with deionized water and ethanol before surface functionalization. After a subsequent wash, an alkanethiol self-assembled monolayer on the gold film was prepared by soaking the probe in an ethanolic solution of 11-mercaptoundecanoic acid (MUA) (1mmol/L) at room temperature for 12 hours to immobilize a layer of capture anti-IgG onto the surface of the probe. Then, the probe was immersed into an aqueous solution containing 1-ethyl-3-(3-dimethylamino-propyl) carbodiimide hydrochloride (EDC, 0.55 mol/L) and N-hydroxysuccinimide (NHS, 0.5 mol/L) for 30 minutes at 4°C to activate the carboxylates of the alkanethiol layer. After activating, the probe was rinsed with deionized water and dried under nitrogen gas stream. Then, the probe was immersed into anti-rabbit IgG solution (0.1 mg/mL in 0.01 mol/L phosphate-buffered saline buffer (PBS buffer, pH 7.4)) for 30 minutes to form stable monomolecular layer. After the rinsing by PBS buffer, 1 mg/mL bovine serum albumin (BSA) was used to deactivate the unreacted groups on the sensing surface. Finally, the functional probe was obtained and the probe can be used for the measurement of specific biomolecule binding.

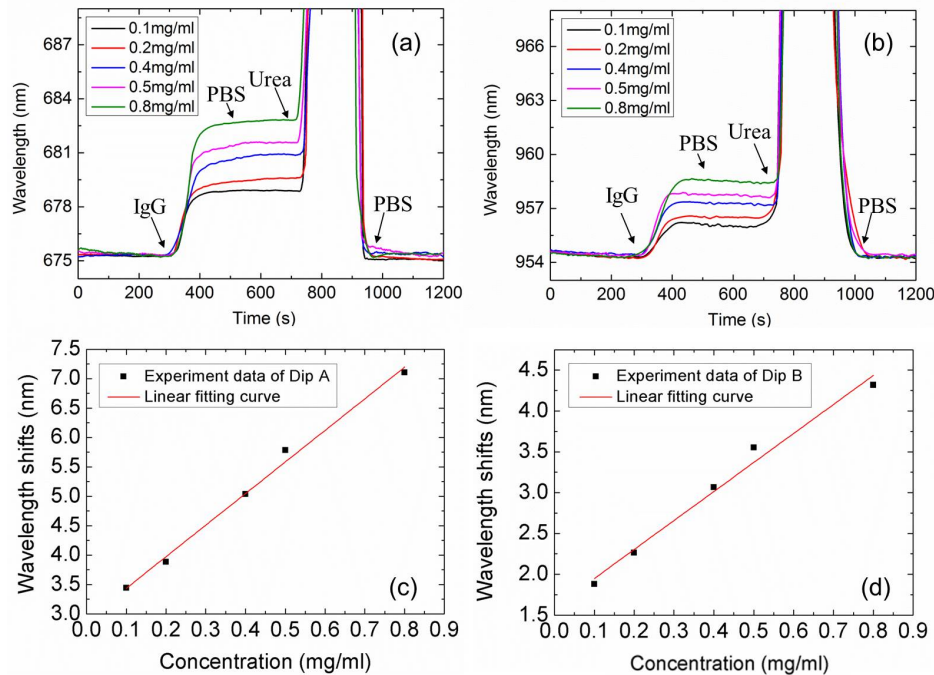


Fig. 6. Real-time biomolecule response with different concentration of IgG samples. (a) Wavelength response of Kretschmann resonance; (b) Wavelength response of Otto resonance; Linear fitting curve of (c) Kretschmann resonance and (d) Otto resonance.

The biological monitoring performance of this dual-channel fiber biosensor was evaluated based on the specific binding of IgG to anti-IgG. IgG samples with different concentrations were prepared in PBS buffer (pH = 7.4) and the laboratory was maintained at 25°C during the test. Before the samples were injected into the flow cell, PBS buffer was introduced to establish the baseline value. The sensorgram of two resonances were monitored by Labview and the experimental data was processed every 2 seconds. Sensorgram of the specific biomolecule binding of two resonances are shown in Fig. 6. The molecular binding will cause the increase of local RI on the sensing surface. Thus, the resonant wavelength increased with time and then reached a steady state after 500 s when the binding was in equilibrium. Figure 6(a) shows that the resonant wavelength of Kretschmann resonance increased due to the injection of IgG, which was consistent with the fact that IgG bound specifically to anti-IgG on the sensing region surface. By using urea solution (8.0 mol/L) to regenerate the biosensor surfaces, IgG samples with various concentrations ranging from 0.1 to 0.8 mg/mL (0.1, 0.2, 0.4, 0.5 and 0.8 mg/mL) were tested. As expected, the response increased as the increasing IgG concentration. Figure 6(b) showed the relationship of the resonance wavelength of Otto resonance with different concentration of IgG samples. As expected, the resonance wavelength of Otto resonance also had red shifts when the concentration increases. However, the SPR wavelength response of Otto resonance was lower than that of Kretschmann resonance, which is consistent with their bulk RI response. As shown in Figs. 6(c) and 6(d), the wavelength shifts of the two resonances both increased linearly with the concentration of the samples.

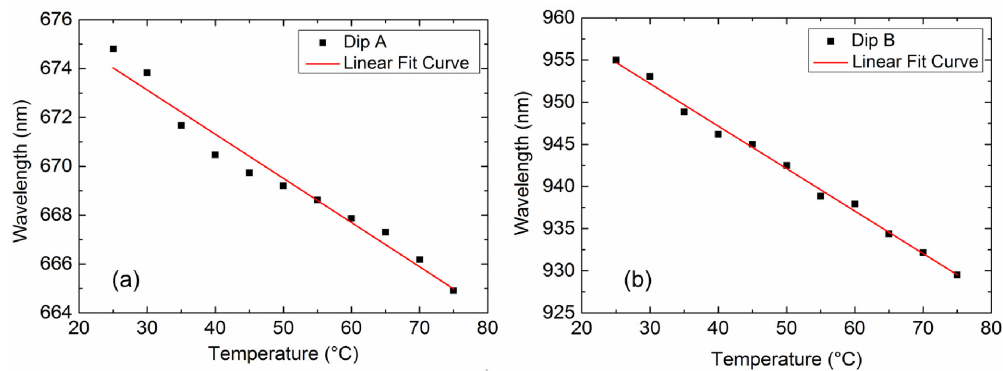


Fig. 7. Temperature response of (a) dip A and (b) dip B.

In the discussions above, we only tested the properties of the sensor at constant room temperature. Due to the effect of temperature on SPR resonance wavelengths, the sensing probe was subjected to external temperature perturbation and the SPR wavelength was tracked at different temperatures. Experimentally, in order to realize the stable temperature test, the temperature was controlled by a heat bath, and a thermocouple was used for temperature calibration. As shown in Fig. 7, we test the temperature responses of both channels with a range from 25 to 75°C. Figures 7(a) and 7(b) illustrate the resonant wavelength variations as the temperature changes in both channels. Experimental data are approximately linear fitted for the test range. The temperature sensitivities of the two channels were estimated from the slope of the fitting curves and were $-0.2 \text{ nm/}^\circ\text{C}$ and $-0.5 \text{ nm/}^\circ\text{C}$, respectively. Due to the high temperature sensitivity, the sensor is only suitable for biochemistry test at the constant temperature condition.

4. Conclusions

In summary, a fiber optic SPR biosensor supporting Kretschmann and Otto resonances in the spectral interrogation scheme was demonstrated by combining ITO and gold films. This sensor possesses two resonances in the visible and in the NIR spectral range, providing a novel multiple spectrum sensing technique with high RI sensitivities. The two resonance dips were attributed to different ways of SPR excitation due to the dispersion of refractive index of ITO layer. Additionally, we investigated the biomolecular sensing feasibility of the sensor when the sensor probe is functionalized by anti-IgG biological molecule. This work provides a new solution to develop wide-spectrum SPR sensors that can be tuned from visible to near infrared range for biological analysis and monitoring, which also can be adapted to other SPR sensors with further investigation.

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