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Study of LSPR Spectral Analysis Techniques on SPR Optical Fiber Sensors

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Abstract

Nanoparticles create localized surface plasmonic resonances (LSPR) with lower surrounding refractive index (SRI) sensitivities than their propagating SPR counterpart, originated in thin films. Historically, LSPR SRI sensitivities enhancements were achieved through spectral analysis methods that focus on unique spectral features. Herein, a study using that methodology was applied on SPR devices resulting in an increased sensitivity to SRI. It was found that by applying the inflection point method on optical fiber SPR sensors resulted in both sensitivity and resolution increments up to 44 and 35 %, respectively, in the SRI range from 1.3333 to 1.4150. Thus, successfully improving sensing capabilities of SPR based optical fiber sensors.

Keywords. Surface Plasmon Resonance, Optical Fiber Sensor, Spectral Analysis Methods.

Type: Research Article

1. Introduction

Surface plasmonic resonances (SPR) represent the collective response of surface plasmon polaritons traveling along a metal–dielectric interface, with propagation characteristics are defined by the materials unique complex permittivities (dos Santos et al. 2021). In addition, the dispersion relation given by Equation (1) must be met (Jatschka et al. 2016).

$$k_x = \frac{2\pi}{\lambda}\sqrt{\frac{n_m^2 n_s^2}{n_m^2 + n_s^2}} \quad (1)$$

where n_m and n_s are the metal and surrounding medium refractive index (SRI), respectively, and λ is the light wavelength. To satisfy this phase-matching conditions, specific light-coupling configurations were created, from the classic prism-based Kretschmann and Otto configurations, to waveguided structures (Caucheteur, Guo, and Albert 2015). Among the last, optical fibers, are of special interest, since they offer a wide range of highly performant and new possible configurations, as conical tips, mirror-facets, tapers, and even gratings, with gold or silver thin films at the sensing area surface (Sypabekova et al. 2019). These configurations, create an intense evanescent wave that penetrates the surrounding medium, allowing them to be among the most relevant and highly performant solutions for chemical and biological sensing applications (Fan et al. 2008; Esfahani Monfared 2020).

In the case of nanoparticle localized SPR (LSPR), the lower SRI sensitivities are caused by the strongest EM field confinement around their surface (Jatschka et al. 2016). This led to studies on possible sensitivity improvements, both physically, with new nanomaterials and geometry developments, as well as on analysis methods, targeting their specific spectral features.

One of these methods is the inflection point (IF) method, as reported by Chen et al. (2017). This method took advantage of the unsymmetrical LSPR band broadening for increasingly higher SRI, taking their first two derivatives and tracking both zeros of the second derivative. This broadening causes the zero at longer wavelengths to present higher redshifts than the band peak. Jeon, Tsalu, and Ha (2019) studied this method for LSPR sensors made from gold bipyramids and gold nanocubes (AuNCs) deposited on a planar glass slide, showing SRI sensitivity increments up to three times. Chen and Liedberg (2014) also applied this method for other nanoparticle geometries, reporting consistent improvements in SRI sensitivity up to 55%. Additional methods, such as curvature analysis were also studied for LSPR bands by Chen and Liedberg (2014) reporting that the peak curvature (related to the 2nd order derivative at peak maximum) shows a linear relationship to the SRI, presenting significant resolution increments.

Such spectral analysis methods targeting SPR sensors were not yet explored. As so, in this work, it is assessed the viability on the application of the IF method for SPR. Thus, combining the strengths of the LSPR spectral analysis techniques with the intrinsically higher SRI sensitivities of SPR. Herein, the study will be conducted by the development of a SPR sensor based of a gold thin film deposited on a decladded section of a multimode optical fiber (MMF) and comparing both SRI sensitivity and resolution.

2. Materials and Methods

A glass MMF with a core/cladding diameter of 600/625 µm was used with a 40 mm decladded section. After exposing the silica core, both ends were polished until an optical quality surface was reached. The sensing section was washed in a mixture of detergent with deionized water in an ultrasonic bath for 10 min. It was then placed in a rotating system inside an electron beam evaporator. Prior to the Au deposition, a 2 nm Cr layer was deposited to improve adhesion whilst not compromising its optical properties (de Almeida et al. 2018). Finally, a 50 nm Au film was deposited in the core-exposed region, resulting in a homogeneous coating.

The measurement setup is shown in Figure 1. A 3D printed sealed fiber holder was developed, allowing full immersion on liquid samples and easy sample removal without physical perturbations. The sensor was illuminated with a tungsten halogen light source and the absorption spectra was measured in transmission, from 200 to 1050 nm, using a spectrometer with a resolution of 1.7 nm. The SRI sensitivity was determined by immersion in samples of ethylene glycol mixed with deionized water, whose RI ranged from 1.3333 to 1.4150, calibrated using an Abbe refractometer with the sodium D line (at 589 nm).

The spectral analysis was carried by the acquisition of ten spectra on each SRI for the complete set of liquid samples. To assure the system integrity, and non-contamination of the gold film, three alternated washings with deionized water and ethanol were performed, guaranteeing that the SPR sensor recovered its initial spectra.

The data processing consisted of the application of a smoothing filter, namely a Savitzy-Golay with 5 points, prior to the derivatives calculation. These were followed by the application of the same smoothing filter. The maxima and minima of the first derivative values were then fitted to a gaussian curve around the peaks.

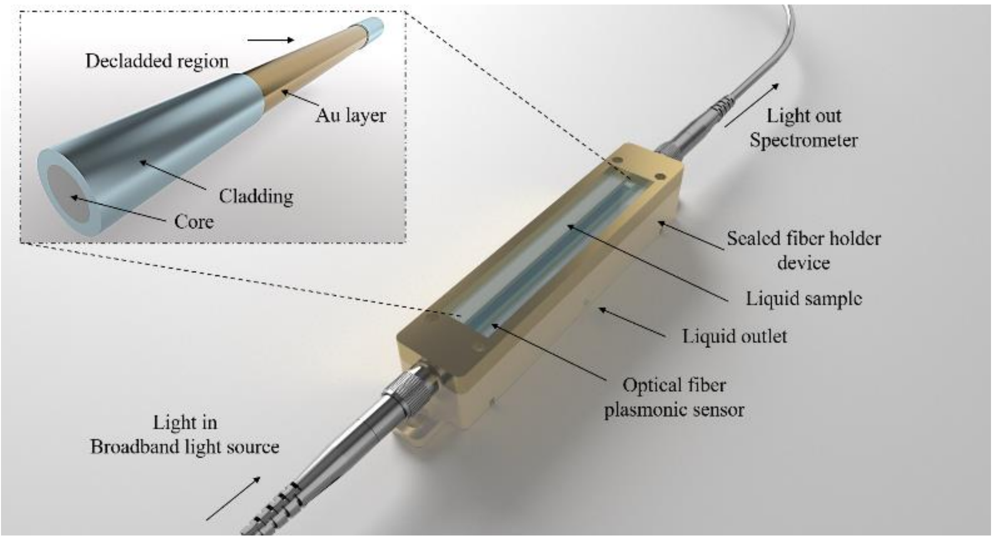

Figure 1: Setup representation of the developed sensor platform for the RI measurements

3. Discussion

The analysis was carried by identifying the band peak (point B), the local maximum (point A) and minimum (point C) of its first derivative, as shown in Figure 2a). This process was carried for all the liquid samples, whose results are presented in Figure 2b).

As expected, the visible broadening towards higher wavelengths, caused by the higher SRI, led to a pronounced increase of the wavelength shift on point C. Additionally, a non-linear SRI sensitivity response was obtained, being the spectral behavior best fitted, not by a linear function, but by a polynomial fitting function of third degree. For SRI values between 1.3333 and 1.4113, the sensitivity in point B changed from 1125 to 5620 nm/RIU, while for point C, an increase from 1621 to 6389 nm/RIU was measured. Regarding point A, an overall lower value for the sensitivity was observed. This is expected since the absorption band broadening counteracts the wavelength shift.

Furthermore, a higher SRI sensitivity, *per se*, does not guarantee better performance. This must be assessed by another figure of merit, Resolution. To account for the different SRI sensitivities, resolution was measured at both RI extremes, by taking a step change in time, as shown in Figure 3.

For each step, ten points were recorded and only the greatest standard deviation (σ) value between the two sides of the step was considered. This resulted in two quite different σ values at both SRI extremes on interval between 1.3333 and 1.3406 to 1.4021 and 1.4113, respectively. The resolution was calculated following Equation (2).

$$R = \frac{2\sigma}{S_n} = \frac{\delta n}{\delta \lambda} 2\sigma \qquad (\mathbf{2})$$

where S_n represents the specific sensitivity and a 2σ standard deviation was chosen. Table 1 summarizes and compares the resolution, SRI sensitivity and σ values at both SRI extremes for the three measurement points (A, B, C).

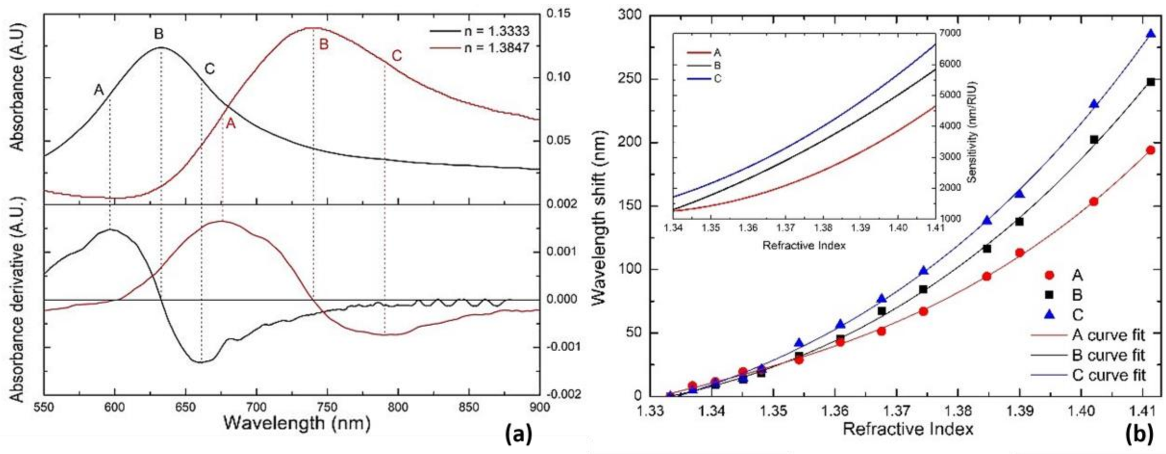

Figure 2: (a) Comparison between absorption spectra for two RI values along with their derivatives. Points A and C represent the local maximum and minimum of the derivative, respectively. Point B is the absorption band peak. (b) Comparison of the wavelength shift caused by the SRI changes for the points considered

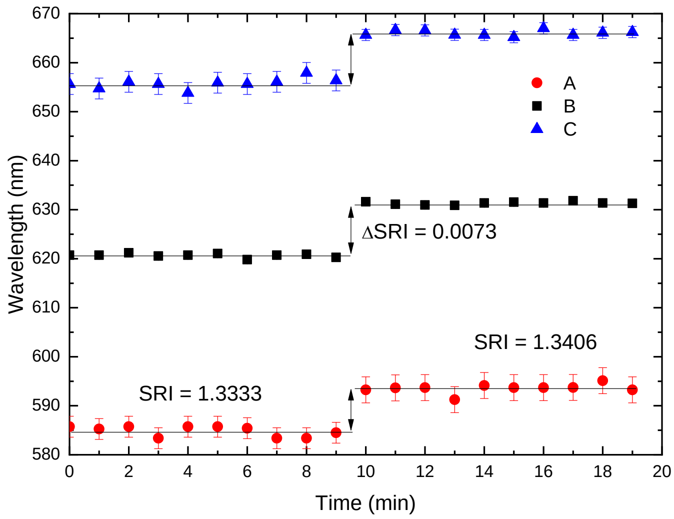

Figure 3: SRI step change on the three considered points of the SPR spectrum using the IF method

Spectral feature	RI step	2σ (nm)	Sensitivity (nm/RIU)	Resolution
Peak (B)	1.3333 –	0.681	1125	6.05×10-4
1st derivative max (A)	1.3406	2.392	1230	1.94×10-3
1st derivative min (C)		1.634	1621	1.01×10-3
Peak (B)		4.297	5620	7.65×10-4
1st derivative max (A)	1.4021 – 1.4113	3.282	4441	7.39×10-4
1st derivative min (C)		3.191	6389	4.99×10-4

Table 1: Comparison of resolution and RI sensitivity between the inflection point and the peak tracking methods

4. Conclusions

By applying the IF method to SPR sensors, it was found that a better SRI sensitivity can be attained, showing improvements from 14 to 44 % in the SRI region from 1.3333 to 1.4150. These results match the magnitude of the SRI sensitivity increments reported on LSPR sensors. As so, it can be concluded that the IF method can successfully be applied not only to LSPR sensors but also to the SPR. Regarding resolution, at the lower SRI region, typical band peak wavelength tracking showed marginally better results, but inside the error margin. Thus, it can be concluded that at lower SRI values there is no advantage in using such analysis. Whereas, in comparison, in the higher SRI region, the IF method resulted in a resolution increment of 35 %.

Additionally, a study for the same optrode configuration with a gold nanoparticle coating could aid the comparison of both types of sensors' performance, thus making this study of more widespread application. Secondly, other types of spectral analysis methods could also be studied in the future, such as curvature analysis to also assess its viability on SPR sensors.

This work contributed to establishing the viability of LSPR spectral analysis methods on SPR sensors, as it was proven that resolution and SRI sensitivity could be enhanced by this analysis. Furthermore, due to the simple and systematic nature of this analysis method, it can also be easily automated in both laboratory and field applications.

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