Comparison of Surface Plasmon Resonance and Localized Surface Plasmon Resonance-based optical fibre sensors

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Abstract. In this work, two of surface plasmon resonance (SPR) and localized surface plasmon resonance (LSPR)-based optical fibre sensors have been successfully developed and cross-compared. With one SPR sensor being coated with a thin layer of gold film and the other gold-nanorods (GNRs), forming a LSPR sensor, both sensors are subjected to various refractive index changes. As a result their sensitivities are measured in the form of resonance wavelength shift as a function of refractive index variation. The results demonstrate that the thin-film coated SPR sensor has much higher sensitivity than that of GNRs coated LSPR sensor but with worse linearity.

1. Introduction
Surface plasmon resonance (SPR) and localized surface plasmon resonance (LSPR) are both powerful tools for label-free biosensing in biochemistry due to their high sensitivity to the refractive index change caused by their interactions with molecules such as DNA or proteins, etc. SPR is known as a phenomenon excited when the frequency of evanescent electromagnetic wave propagating at the metal-dielectric interface is resonant with the oscillation of the surface conduction electrons in metal [1]. LSPR often refers to metallic nanoparticles as it occurs when the frequency of incident photon is resonant with the oscillation of the surface conduction electrons in metal [2].

Traditional SPR sensors are fabricated based on the Kretschmann configuration where a thin noble metal film is coated on a prism [3]. LSPR sensors, on the other hand, are normally fabricated on a chip where noble metal nanoparticles are coated on a substrate such as glass slide [4]. However, most of the conventional SPR and LSPR sensors require bulky and expensive optical equipment and data analysis instrument and, hence, are only can be used in a laboratorial environment. Compared to the traditional SPR and LSPR sensors, fibre-optic based SPR and LSPR sensors have shown advantages, such as requiring small sample volume due to the small sensing tip, using simplified optical design and showing potential to be disposable and the capability for remote sensing. Compared to SPR technology, LSPR has its own advantages by being able to control/optimize the sensitivity of LSPR sensor through the change of the sizes and shapes of nanoparticles [5]. This work is aimed to explore the differences between fibre-optic based SPR and LSPR sensor designs, therefore their corresponding sensing capabilities when they both are subjected to refractive index changes. To date, little comparison was made between SPR and LSPR sensors [6-7] and it is the first time that, to the
knowledge of the authors, a cross-comparison is made between SPR and LSPR sensors based on optical fibre.

Therefore, in this work, we studied the characteristics both of fibre-optic based SPR and LSPR sensors by comparing their fabrication and sensitivity to bulk refractive index (RI) change. The SPR sensor was constructed by coating a thin gold film on the unclad core of an optical fibre. To make a comparison with SPR sensor, GNRs were synthesized and immobilized on the same structure of an optical fibre to fabricate LSPR sensor. The sensitivity study was performed by dipping the sensors into solutions with different refractive index, and monitoring the corresponding resonance wavelength shift. The results show that optical fibre based SPR sensor has much higher bulk refractive index sensitivity than LSPR sensor but with worse linearity.

2. Experimental set-up

Prior to the experimental tests, a SPR sensor was constructed by coating a thin gold film on the surface of an optical fibre with its cladding being removed. To make a LSPR sensor, GNRs were first synthesized and then immobilized on the surface of an optical fibre with cladding being removed. Subsequently both sensors were dipped into solutions with different refractive index, their corresponding resonance wavelength shifts were monitored to allow the cross-comparison of the sensor sensitivities observed.

2.1. Preparation of SPR sensor

A piece of 10 cm of multimode (600µm) optical fibre was chosen specifically to allow the easy removal of fibre cladding of about 1cm length at one end. Subsequently the fibre was finely polished at both two end surfaces. To prepare SPR fibre probe, 50 nm thick of gold film was coated on the surface of unclad portion by using a sputter coater. In order to make a reflective optical fibre sensor probe, a thin silver layer was coated onto the end surface of the fibre to allow the reflection of the incident light.

2.2. Preparation of LSPR sensor

2.2.1. Synthesis of GNRs

GNRs were prepared by following the method reported by Nikoobakht et al [8]. Firstly, seed solution was prepared by mixing 5 mL of 0.2 M CTAB solution with 5 mL of 0.5 mM HAuCl4 solution. To the stirred solution, 600 µL of 0.01 M NaBH4 was added, which resulted in the formation of a brownish yellow solution. After additional 2 min vigorous stirring, the seed solution was kept at room temperature (25°C) without disturbing for at least 2 h before use. To prepare gold nanorods solution, 25 mL of 0.2 M CTAB solution was added to 0.5 mL of 0.01M AgNO3 solution and 25 mL of 0.001 M HAuCl4 solution respectively. To the mixed stirred solution, 350 µL of 0.0788 M ascorbic acid solution, which works as a mild reducing agent, was added and changed the color of growth solution from dark yellow to colorless. To grow GNRs, 60 µL of seed solution was added to the growth solution at about 30 °C. The color of the solution was gradually changed within 20 min. The solution was kept at 30 °C for 24 h. Excess amount of CTAB was removed by twice careful centrifugation at 7000 rpm for 20 minutes each time. Finally the GNRs were dispersed in DI water.

2.2.2. Preparation of LSPR sensor

Prior to the immobilization of GNRs onto the surface of an optical fibre, a piece of 10 cm of multimode (600µm) optical fibre was chosen specifically to allow the easy removal of fibre cladding of about 1cm length at one end. Subsequently the fibre was finely polished at both two end surfaces. Prior to the immobilization of GNRs onto the surface of the unclad section of the fibre, the fibre was cleaned by piranha solution (H2O2: H2SO4; 30%:70%) for 30 minutes. (It should be noted that this solution is extremely dangerous and thus was handled with extreme care). After a thorough rinse with DI water, the optical fibre was placed in an oven set at 110°C for 2 h. The fibre was then immersed in
5% mercapto-propyl-trimethoxysilane (MPTMS) ethanol solution for 5 h before being sonicated in ethanol for 3 minutes. Subsequently it was thoroughly rinsed with ethanol and DI water to remove unbound MPTMS and to be blow-dried using N₂. The mercaptosilane modified optical fibre was incubated in the GNRs solution overnight to enable the immobilization of GNRs onto the fibre surface. In order to make a reflective optical fibre sensor probe, a thin silver layer was coated onto the end surface of the fibre to reflect the incident light back.

2.3. Solutions with different refractive index
In order to test the sensor performance, solutions with different refractive index were prepared, ranging from 1.333 to 1.423, through the use of water and mixed solvents of methanol, ethanol and toluene at different ratios. A refractometer purchased from Fisher Scientific was used to measure the refractive index of testing solutions.

2.4. Experimental set-up
Figure 1 (a) shows the schematic diagram of a sensor system set up to evaluate the sensor performance. As shown in the diagram, light from a white light source is coupled to the sensor probe, SPR probe or LSPR probe, through a 2x1 fibre coupler. The sensor probe is dipped into a solution with a known refractive index and the reflected signal is captured by a mini-spectrometer (Ocean Optics Maya 2000pro), which is connected to the other side of the coupler. Thus the signals obtained could be displayed and monitored by a computer connected to the mini spectrometer. Figure 1(b) shows the photo of the bench-top sensor system setup.

![Figure 1. (a) Schematic diagram of the system. (b) Photo of the experimental setup.](image)

3. Experimental results and discussion
GNRs possess two plasmon resonance bands, with one being the transverse plasmon wavelength (TPW) at about 520 nm and the other the longitudinal plasmon wavelength (LPW) appearing between the visible and near infrared wavelength range and varying with the aspect ratio (length to width) [9]. It is known that the LPW is highly sensitive to refractive index changes and the sensitivity increases with the increase of the aspect ratio of the GNRs while the TPW is insensitive to refractive index change [10]. Therefore, in this work, LPW shift of the GNR-coated sensor was specifically chosen to make a comparison with the SPR wavelength shift of the gold-film coated sensor. The average aspect ratio of the GNRs synthesized for this experiment is about 3.5. The advantage of using LSPR sensor is that it can be fabricated easily through a chemical process rather than using expensive equipment, such as sputter coater or evaporator, as used for the thin-film coated SPR sensor preparation.

Figure 2 shows clearly both the reflection mode of the gold-film coated SPR sensor, in Figure 2(a), and absorbance mode of the GNRs-coated LSPR sensor, in Figure 2(b), as a function of refractive index.
index change. The shift of dip in SPR sensor spectra and peak of LPW in LSPR sensor spectra were measured as a function of refractive index change. When the refractive index varies from 1.333 to 1.423, a total wavelength shift of 310 nm was observed for SPR sensor and 70 nm for LSPR sensor. It indicates that the refractive index sensitivity of SPR sensor is about 3444 nm/RIU, which is more than four times higher than that of the LSPR sensor, of which the sensitivity is about 778 nm/RIU. The results obtained from LSPR are similar to what have been reported by other researchers based on a chip structure [7].

![Overlapping spectra of (a) gold film based SPR sensor and (b) gold nanorods based LSPR sensor with increase of refractive index.](image)

Figure 2. Overlapping spectra of (a) gold film based SPR sensor and (b) gold nanorods based LSPR sensor with increase of refractive index.

Figure 3 summaries the peak/dip wavelength changes of the sensors with the change of refractive index. It is noticeable that the sensitivity of SPR sensor only has a good linearity at a short refractive index range from 1.33 to 1.39. When the refractive index is higher than 1.39, the dip wavelength versus refractive index increases more dramatically, which means the SPR sensor becomes more sensitive. The LSPR sensor, on the other hand, has a much better linearity than the SPR sensor through the whole RI range.

![SPR versus LSPR wavelength shift with refractive index change.](image)

Figure 3. SPR versus LSPR wavelength shift with refractive index change.
4. Conclusion
In this work both gold-film coated SPR sensor and GNRs-coated LSPR sensor have been successfully fabricated, evaluated and cross-compared. When the aspect ratio of the GNRs is around 3.5, it can be concluded that SPR sensor has demonstrated to be more sensitive than that of the LSPR sensor when the solution refractive index changes. However the LSPR sensor has shown several advantages including ease of fabrication and linear performance. In addition, LSPR sensor sensitivity can potentially be tuned through the change of the GNR dimensions, such as aspect ratio, to allow an optimized sensor to be created for some specific sensor applications.

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