Plasmonic-enhanced fluorescence emission using D-shape microstructured optical fiber

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Abstract. Highly sensitive side-polished D-shaped optical fiber sensors have been fabricated based on surface plasmon resonance (SPR) technology. Current techniques in plasmonic-enhanced total internal reflection microscopy (TIRM) and evanescent wave microscopy, although advantageous, require cumbersome set-ups and encompass large coupling losses. A gold coated D-shaped optical fiber was demonstrated to provide fluorescence enhanced spectroscopy. Comparison was made between a gold coated and uncoated D-shaped microstructured optical fiber (MOF) with respect to excitation of Rhodamine B (Rh B). Results highlighted improved fluorescence emission intensity and heightened sensitivity in fluorescence spectroscopy in the gold coated device, indicating potential in enhanced bio-imaging applications.

1. Introduction

SPR has been vastly explored for optical sensing applications [1]. Optical fibers, notably, have provided a means of miniaturization for SPR sensors. In particular, a side-polishing method, where the cladding of the optical fiber is removed locally, rendered the evanescent field of the optical fiber’s guided mode accessible. The side-polished D-shaped optical fiber was further coated with a thin gold film allowing its support of surface plasmon waves (SPW) [2-3]. Additionally, since the refractive index of the adjacent medium (analyte) drastically alters the SPW’s propagation constant, coupling

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between the fiber mode and SPW is highly dependent on the analyte, enabling the fabrication of highly sensitive side-polished D-shaped optical fiber sensors [4-5].

Apart from applications in optical sensing, SPR has enabled heightened spatial resolution and background suppression of fluorescent labels in plasmonic-enhanced TIRM [6] as compared to conventional TIRM [7]. The numerous lenses and filters for guidance and focusing of light, however, render the set-up bulky and inflexible. Furthermore, background auto-fluorescence was inevitably elicited due to propagation of excitation light through the glass objective. Nevertheless, despite further modifications made in auto-fluorescence mitigation, via avoidance of propagating excitation light through the objective [8], the set-up remains equally cumbersome. Additionally, planar waveguides have also been employed in evanescent wave fluorescence microscopy. Unlike TIRM, excitation is confined at the sample surface in contact with the illumination platform, enabling study of cell surface events and morphology [9]. Coupling of the excitation source to the planar waveguide via manual alignment with optical fibers, however, elicits huge losses.

D-shaped optical fibers, on the contrary, provide a less cumbersome alternative to the illumination platform due to the flexibility and minute size of optical fibers. Furthermore, coupling of excitation sources directly into optical fibers diminishes losses. In this paper, a novel fiber device for plasmonic-enhanced fluorescence spectroscopy, structured upon a D-shaped optical fiber, is proposed and demonstrated. Comparison was made between a gold coated and uncoated D-shaped optical fiber, where different forms of fluorescence excitation modes are offered, namely SPWs and evanescent waves correspondingly. The presence of the gold coating demonstrated an improvement in fluorescence emission intensity and heightened sensitivity in fluorescence spectroscopy. In addition, results were indicative of increased efficiencies in energy coupling from SPWs to fluorescence molecules as compared to that by evanescent waves. Furthermore, the gold coated D-shaped optical fiber showed higher accuracy in data projection.

2. Methodology

An organic fluorescence, Rh B, was separately excited by evanescent waves and SPWs via a gold coated and an uncoated D-shaped optical fiber respectively. The resultant emissions were analysed and compared. The optical fiber, an all solid microstructured optical fiber (MOF) described in [10], was embedded in a grooved silica block and subsequently polished till its photonic crystal core. The resultant D-shaped MOF is illustrated in Fig 1(a). An identical D-shaped MOF was further coated with a thin gold layer of an approximate 35 nm thickness, and is shown in Fig 1(b).

![Figure 1](image-url)

**Figure 1.** D-shaped MOFs (a) uncoated, illustrating polished depth and (b) coated, highlighting coated thin gold film.

The experimental set-up, as depicted in Fig. 2, was utilised in the detection of fluorescence emission for both the coated and uncoated D-shaped MOFs. A laser of wavelength, $\lambda = 532$ nm was butt-coupled into the D-shaped MOF via a translation stage. Collected signal was guided through a fiber optic cable to a PC-linked spectrometer (Ocean Optics, Maya 2000) for spectral analysis. Position of the objective lens was maintained for the remaining collection of emission data. A droplet of Rh B, overlapping the D-shaped region, was dripped onto the surface of the silica block, and its
emission was subsequently collected. Respective emission spectra were obtained for Rh B of concentrations $10 \, \mu\text{M}$, $35 \, \mu\text{M}$, $50 \, \mu\text{M}$, $75 \, \mu\text{M}$, $100 \, \mu\text{M}$, $350 \, \mu\text{M}$ and $500 \, \mu\text{M}$.

![Diagram](image1)

Figure 2. Experimental set-up for detection of fluorescence emission from gold coated D-shaped MOF. An identical set-up was utilised for the uncoated D-shaped MOF.

3. Results and Discussion

Fluorescence emission spectra for both gold coated and uncoated D-shaped MOFs were studied and further contrasted. Comparisons were made on the emission spectra, the peak emission wavelengths as well as the peak emission intensities. The heightened fluorescence emission intensity and fluorescence spectroscopy sensitivity under surface plasmon excitation were consequently highlighted.

3.1. Comparison of fluorescence emission spectra

Fluorescence emission spectra resided between 550 nm and 770 nm for both gold coated and uncoated D-shaped MOFs and are shown in Fig. 3(a) and 3(b) correspondingly. Average peak emission wavelengths of 597 nm and 587 nm were further calculated respectively and indicated a red shift in the presence of a thin gold film. Emission at a longer wavelength, for the gold coated D-shaped MOF, signifies a lower emission energy therefore implying a lower required excitation energy. This demonstrated reduced energy losses to the surrounding and thus increased efficiency in energy coupling from SPWs, elicited by the thin gold film, to Rh B molecules.

![Graph](image2)

Figure 3. Fluorescence emission spectra of (a) uncoated and (b) gold coated D-shaped MOFs.
3.2. Comparison of peak emission wavelength

A relationship between peak emission wavelength shifts with respect to changing Rh B concentrations was drawn for both gold coated and uncoated D-shaped MOFs to provide a lucid comparison.

As illustrated in Fig 4, it is evident in both cases that the peak emission shifts to higher wavelengths with increasing Rh B concentrations. This phenomenon is deduced due to re-absorption of emissions. Since excitation and emission follows Stokes shifting, the emission energy is lower as compared to that of excitation. Emission energy post re-absorption, therefore, was constantly being reduced after each excitation-emission step [11]. The lower emission energy consequently resulted in a longer emission wavelength. In short, an increase in Rh B concentration raised the probability for emission reabsorption, essentially reducing the energy of emission and hence resulted in a shift of peak emission to higher wavelengths.

Conversely, a distinctive difference was observed between the gradients of the two plots. A sharper rise in wavelength with respect to the increasing Rh B concentration, as indicated by the gradient, was shown by the gold coated D-shaped MOF. The steeper gradient demonstrates a higher sensitivity in fluorescence spectroscopy, indicating improved coupling of core energy to the evanescent field by SPWs. In addition, the larger R-square value of 0.9926, for the gold coated D-shaped MOF, was indicative of its higher accuracy in projection of data.

![Graph showing comparison of peak emission wavelengths](image)

**Figure 4.** Comparison of shifts peak emission wavelengths with change in Rh B concentration, between gold coated (blue) and uncoated (red) D-shaped MOFs.

3.3. Comparison of peak emission intensity

Further study was made on the peak emission intensities with respect to Rh B concentration. Fig. 5 portrays a similar trend for both gold coated and uncoated D-shaped MOFs, where initial increment of Rh B concentration (10 μM to 100 μM) led to a rise in peak emission intensity whereas further increment resulted in a drop. During the initial increment, increasing amounts of Rh B molecules became available for excitation; the amount of Rh B molecules was thus the limiting factor. Upon further increment, two phenomena occur concurrently. First, a maximum rate of excitation was attained, eliciting a saturation of Rh B emission; here the excitation source was the limiting factor. Second, the further increment in Rh B concentration caused a larger proportion of Rh B molecule not being in contact with the SPWs or evanescent waves, amplifying the probability of collisions between
excited and non-excited Rh B molecules. This resulted in higher efficient quenching of excited Rh B molecules via non-radiative energy transfer to non-excited Rh B molecules. Hence, the likelihood of actual emission from an excited Rh B molecule is diminished, reducing the overall emission. The collective effect of the two described phenomena, thus, grounds the drop in peak emission intensity [12].

Emission intensities, on the contrary, were distinctively different. Notably, emission intensity was easily influenced by experimental factors, namely the size of the fluorescence droplet as well as the alignment at the butt-coupled input. Experimental data were therefore collected and averaged over three data sets to minimise the influence of such factors. It is hence evident that the 2 fold higher overall fluorescence emission intensity, for the gold coated D-shaped MOF, was contributed by plasmonic enhancements. In addition, fluorescence excitation at the D-shaped surface with emission collected at the fiber end face was also conducted on the uncoated D-shaped MOF. Peak emission intensity, in this case, was several orders lower.

Furthermore, Rh B concentration for optimum peak emission was higher for the gold coated D-shaped MOF at 1.90 M as compared to 1.61 M. This indicates saturation of excitation at higher Rh B concentrations, implying a higher maximum rate of excitation as provided by the SPWs. A higher efficiency of energy transfer from SPWs to Rh B molecules is again demonstrated.

![Graph showing peak emission intensity vs RhB concentration](image)

**Figure 5.** Comparison of peak emission intensity with change in Rh B concentration, between gold coated (blue) and uncoated (red) D-shaped MOFs as well as excitation at D-shaped surface (black).

### 4. Conclusion

Plasmonic-enhanced fluorescence spectroscopy has been demonstrated on a gold coated D-shaped MOF. Results highlight the improved fluorescence emission intensity as well as heightened sensitivity in fluorescence spectroscopy due to plasmonic enhancements. Results also indicated higher efficiencies in energy coupling for SPWs to fluorescence molecules as well as showed higher data projection accuracy in the plasmonic-enhanced device.

These exhibit the potential of plasmonic-enhanced D-shaped MOFs as compact illumination platforms with high coupling efficiencies, for applications in improved bio-imaging with superior histogram output.
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