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Enhancing Label-Free Biochemical Sensing via Graphene Oxide Layer Deposition on Dual Resonance Peak Long Period Gratings

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Abstract: This research introduces a novel label-free graphene oxide-coated dual-peak long-period grating sensor for measuring protein concentrations. It achieves high sensitivity (22 nm/(g/mL)) and a low limit of detection (0.9 μg/mL), demonstrating extremely high potential for fiber optic biosensor development. © 2023 The Author(s)

1. Introduction

The detection of biological species and the accurate measurement of their concentration is an extremely important process in applications such as those in healthcare, drug discovery in the pharmaceutical sector, environmental monitoring, and clinical analysis [1]. Label-free biochemical sensing has revolutionized the field of biosensing by enabling the detection and analysis of biomolecules without the need for molecular labels or tags. This approach offers numerous advantages, including real-time monitoring, simplicity, and cost-effectiveness. Various sensing platforms have been developed to achieve label-free detection, among which Long-Period Gratings (LPGs) have emerged as versatile and highly sensitive optical transducers for such biosensing applications [2].

LPGs are optical fiber-based sensors that exploit the coupling between the forward propagating core mode and co-propagating cladding modes of the fiber to create resonant peaks in the transmission spectrum. These resonant peaks are highly sensitive to changes in the surrounding refractive index (RI), making LPGs ideal for biosensing applications. One of the significant challenges in conventional LPG-based biosensors is achieving higher sensitivity without compromising the specificity. Shu et al. [3] have shown that higher order cladding modes exhibit parabolic properties and as such, there is a group of dispersion turning points that exits in the phase matching curves of these particular higher order modes. Due to this, two resonance peaks of the same cladding mode can be realised that portray wavelength shifts of different signs under the same external RI perturbation. These Dual Resonance Peak LPGs (DLPGs) are extremely sensitive to external RI variations compared with a normal resonance peak associated with lower order modes of a LPG, enabling the detection of analytes at lower concentrations.

Graphene oxide (GO), a two-dimensional carbon-based material, has gained significant attention in recent years due to its exceptional physicochemical properties [4]. The deposition of GO layers on DLPGs introduces a novel dimension to label-free biochemical sensing in overcoming the above mentioned challenges faced by conventional LPG-based sensors. Firstly, the GO layer can be easily functionalized with various biomolecules, enabling specific recognition and binding of target analytes. Secondly, the strong light-matter interaction between the guided core mode and the GO layer enhances the sensitivity of the biosensor, enabling detection of analytes at extremely low concentrations. Additionally, the presence of GO modifies the refractive index profile of the LPG based on the analyte dependent RI of the GO layer, leading to a shift in the resonance peaks, which can be precisely measured to determine the concentration of the target analyte.

In this context, this paper aims to explore the potential of enhancing label-free biochemical sensing through the deposition of GO layers on DLPGs. After discussing the fabrication process and its sensing mechanism, the protein binding affinity and the sensitivity of the proposed GO coated DLPG sensor platform is presented by analysing the transmission spectra under varying aqueous concentrations (0.2 g/mL to 1.5 g/mL) of Bovine Serum Albumin (BSA), one of the most widely used proteins in biotechnology applications.

By combining the unique properties of GO and the versatile sensing capabilities of DLPGs, we hope that this hybrid innovative sensing platform opens up exciting possibilities for sensitive and selective detection of biomolecules, contributing to the advancement of diagnostics, biomedical research, and environmental monitoring.

2. Sensing Principle

In order to describe the working principle of the developed GO coated DLPG sensor and also to explain the formation of the dual resonance peaks of the LPG, a $\Delta n_{eff}(\lambda)$ function can be defined based on the phase matching conditions of a LPG [5].

$$\Delta n_{eff}(\lambda) = n_{eff,co}(\lambda) - n^{v}_{eff,cl} - \lambda/\Lambda \tag{1}$$

where $n_{eff,co}(\lambda)$ is the effective RI of the core mode, $n^{v}_{eff,cl}$ is the effective RI of the v^{th} order cladding mode, λ is the wavelength, and Λ is the period of the LPG structure. The roots of the equation $\Delta n_{eff}(\lambda)$ =0 determine the resonant wavelengths of the LPG. In [5], Gu et al. have shown that for a given resonance wavelength, $\Delta n_{eff}(\lambda)$ takes a parabolic shape, which explains the dual peak formation for higher order cladding modes of a LPG. Most importantly, they have also shown that by making the grating period of a LPG smaller, dual resonance peaks can be achieved in the operational wavelength region of current optical spectrum analyzers ($<$ 2000 nm), which forms the basis behind the fabrication of DLPGs used in this work as described in the next section. As can be seen from equation (1), the resonance wavelengths of a thin film coated DLPG is a function of $n_{eff,cl}$, which comprises of the cladding RI, as well as the RI index of the coated thin film layer, in this case, GO. When the GO coated region of the DLPG interacts with a bioanalyte like BSA as shown here, RI of the GO layer changes, which leads to pertubations in the centre wavelengths of the respective resonance loss bands. This forms the sensing principle of the GO thin film coated DLPG sensors developed in this work.

3. Sensor Fabrication and Characteristics

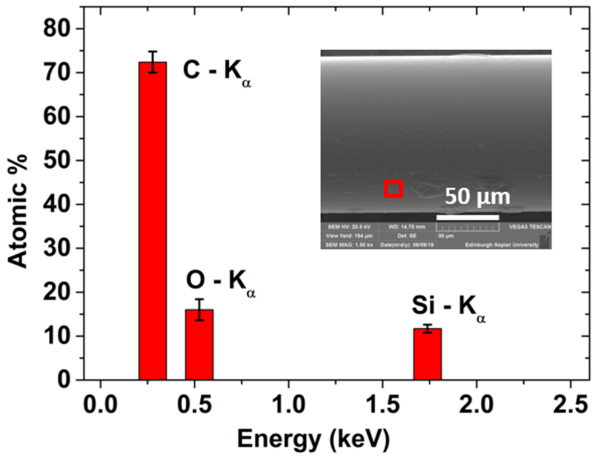

Fig. 1: SEM image and EDX spectrum (of the red box area) of the GO coated fiber surface of the DLPG.

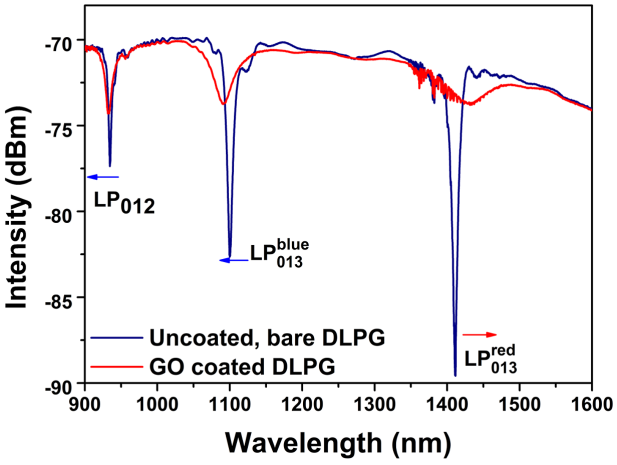

Fig. 2: Transmission spectra of uncoated and GO coated DLPG.

The DLPG with a grating period of 150 µm and 30 mm length was inscribed on a B/Ge co-doped single mode photosensitive fiber (from Fibrecore, UK - PS 980 nm), with a cut-off wavelength of 850 nm, by exposing to the UV light from a 248nm KrF excimer laser through a 150 µm metal amplitude mask. This specific fiber and the amplitude mask were chosen to realise the DLPG resonance of the higher order cladding modes within the operating wavelength region of the OSA (this being from 700 nm to 1650 nm). The pulse energy was set at 10 mJ and a pulse frequency of 100 Hz was used in this DLPG inscription process that was optimised to allow a UV light exposure time of 6 minutes after the previous optimisation process was carried out. After the inscription process, the fabricated DLPG was annealed at 100 °C for 3 hours to stabilize its optical properties. It should be noted that, by using these DLPG fabrication specifications, dual resonance has been achieved without any cladding etching being required.

A drop casting technique was used to deposit GO thin film layers on the surface of the DLPG, as fabricated above, to create the GO-coated fiber optic biosensor probes used in this work. To do so, 5 mg of GO flakes, synthesised via a modified version of the Hummer's method outlined in [6], was dissolved in 10 mL of DI water to prepare the GO aqueous dispersion with a concentration of 0.5 mg/mL. Then the GO aqueous dispersion was sonicated for 1.5 hours before being centrifuged for another 20 minutes at 3000 rpm. After this centrifugation process, the supernatant was used to achieve a high percentage of single layered GO flakes in the solution. Afterwards, 1 mL of the supernatant was diluted with 5 mL of DI water to achieve the concentration required to realise an optimum thickness of the GO overlay on LPG structures using the drop casting method. Fig. 1 presents a Scanning

Electron Microscope (SEM) image of the GO-coated DLPG, accompanied by its corresponding Energy Dispersive X-ray (EDX) analysis graph. Additionally, Fig. 2 illustrates the transmission spectra of the developed sensor probe before and after the deposition of the GO thin layer (post-annealing). These results indicate the successful attainment of a GO thin layer of approximately 414 nm in thickness (calculated from SEM images of the fiber cross-section) on the DLPG fiber surface.

4. Performance Analysis of the GO coated DLPG Probe for BSA Concentration Variations

To study the performance of the GO-DLPG probe in measuring BSA concentrations, the sensing area of the probe was incubated in aqueous solutions of five different BSA concentrations of 0.2 g/mL, 0.5 g/mL, 0.8 g/mL, 1.0 g/mL, 1.2 g/mL, and 1.5 g/mL at room temperature (22 °C) using the experimental setup described in [6]. The variations in the transmission spectra of the GO-DLPG sensor probe are shown in Fig. 3.

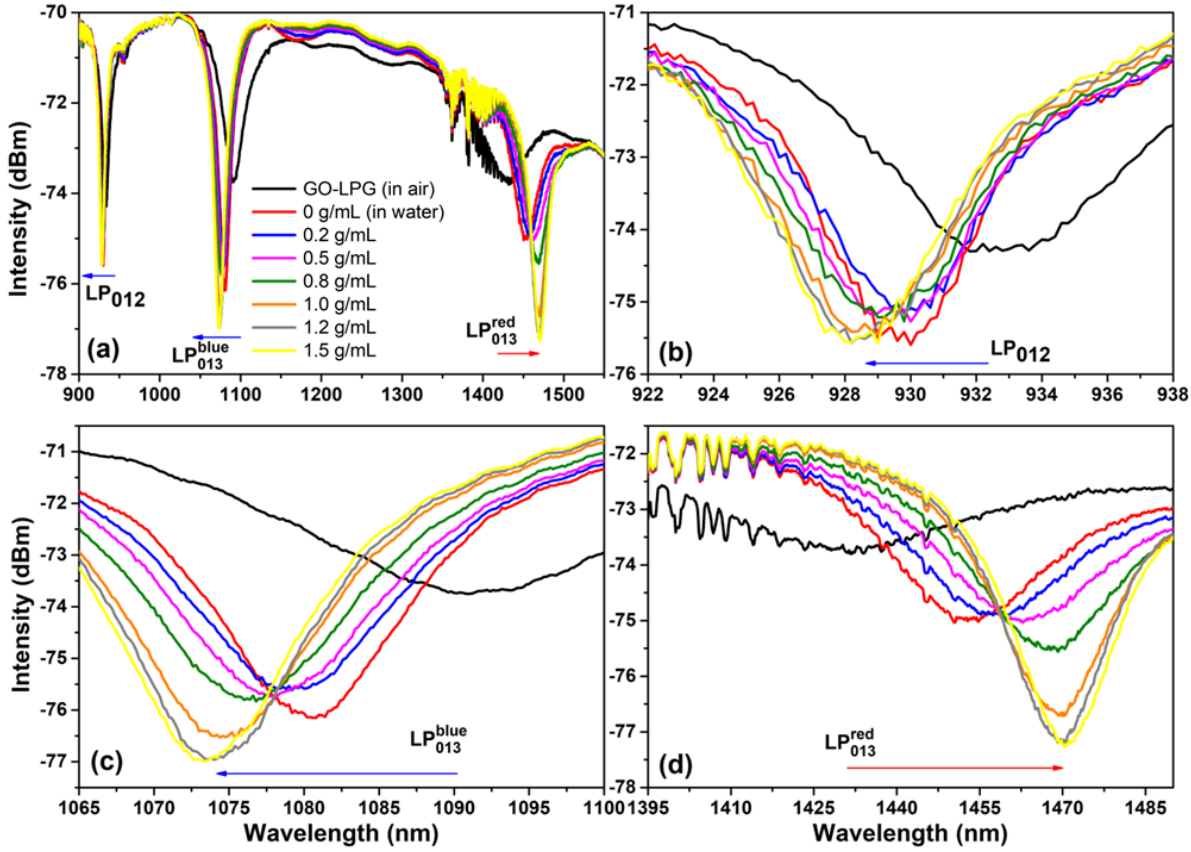

Fig. 3: (a) Transmission spectra of GO coated DLPG measured in different BSA concentrations (b) Zoomed evolution of LP_{012} mode (c) Zoomed evolution of LP_{013}^{blue} peak (d) Zoomed evolution of LP_{013}^{red} peak.

As can be seen from the GO-DLPG response above, the blue shift of the LP_{012} resonance peak was noticed to be less than 2 nm in contrast with a blue shift of 7.4 nm and a red shift of 17.4 nm recorded by the LP_{013}^{blue} and LP_{013}^{red} peaks, respectively, in the same region of increasing BSA concentrations.The enhanced sensitivities of the centre wavelength of the resonance loss bands, with variations in BSA concentration, are attributed to the enhanced interaction between light and matter. This interaction occurs due to the appearance of dual-peak resonances in higher order cladding modes at the interface of the cladding-GO thin film overlay. The observed optical perturbations in the LP_{013} cladding mode are caused by the GO-BSA interactions that occur when the sensor probe is immersed in BSA solutions.

Fig. 4 depicts the sensitivity curves of three different sensors: a GO coated single resonance peak LPG (LP_{08} cladding mode) with approximately the same GO layer thickness, an uncoated bare DLPG (fabricated and characterized using the same methods as described earlier), and the GO coated DLPG sensor probe. The curves represent the resonance wavelength shift as a function of increasing BSA concentrations ranging from 0.2 g/mL to 1.5 g/mL. For all the resonance loss bands of the GO-coated sensor probes, except for the bare DLPG dual-peak separation curve, two sections of the wavelength shift curve can be observed. A linear increment in wavelength shift is observed for BSA concentrations ranging from 0.2 g/mL to 0.8 g/mL. However, at higher BSA concentrations (above 1.0 g/mL), the wavelength shift curves of the GO-coated sensors exhibit a saturation point, demonstrat-

ing a parabolic nature. The observed saturation at higher BSA concentrations indicates that the available binding sites on the GO surface for BSA molecules become populated, leading to a saturation of both covalent and non-covalent interactions between BSA molecules and functional sites of the GO layer. Conversely, this phenomenon does not apply to the uncoated DLPG, where the wavelength shift is solely dependent on the external refractive index change.

A highest sensitivity of 22 nm/(g/mL) was achieved by the dual peak separation of the GO-coated DLPG sensor probe in the BSA concentration region from 0.2 g/mL to 0.8 g/mL, which led to a Limit of Detection (LOD) of 0.9 µg/mL based on the highest resolution of the OSA (Yogokawa 6370C) used to conduct the experiment. It was also noted that the achievable LOD is 11 times better than that of a GO-coated conventional single peak LPG sensor probe and 5 times better than that of an uncoated DLPG sensor probe. This result underscores the superior sensing capabilities of GO and the enhanced external RI sensitivity achieved by dual resonance peaks, in contrast to the single resonance peaks of lower order long-period grating (LPG) modes, demonstrating the potential of GO coated DLPGs for biosensing applications.

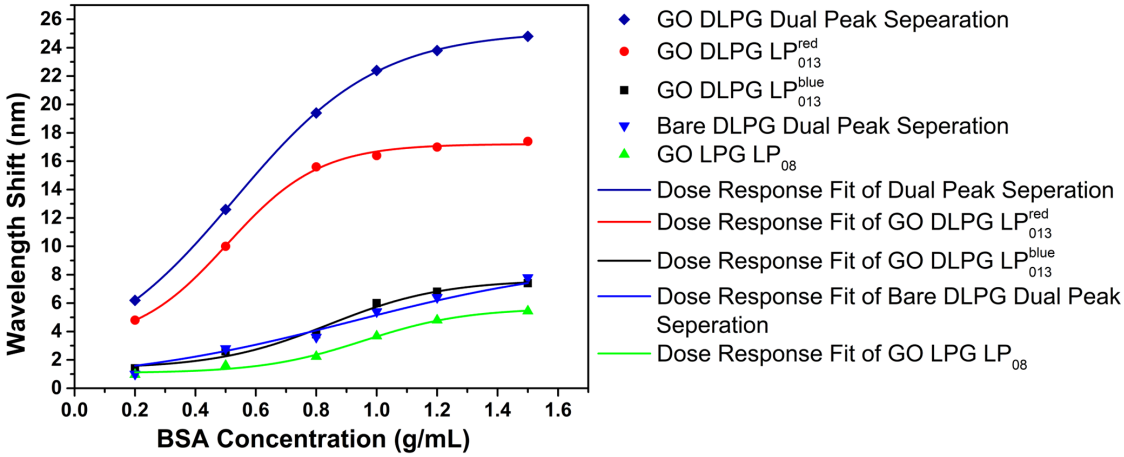

Fig. 4: Wavelength shift of the sensor probes with varying BSA concentrations

5. Conclusions

This paper presents a label-free sensor for measuring BSA concentrations using a GO-coated DLPG, at the same time discussing the sensor fabrication steps and the system performance (under varying BSA concentrations) in detail. A drop casting technique was used to deposit the GO thin film overlays of ∼400 nm on the fiber optic sensor probes under discussion. The GO-coated DLPG demonstrates significantly higher sensitivities compared to a GO-coated LPG and an uncoated DLPG, achieving a highest sensitivity of 22 nm/(g/mL) for BSA concentration measurements. The LOD for BSA concentration is 0.9 µg/mL, outperforming the GO-coated LPG by a factor of 11 times and the uncoated DLPG by 5 times. These promising results indicate the excellent potential of GO combined with DLPGs as a sensing material for fiber optic biosensor development, owing to its rich surface chemistry. Additionally, the GO-coated DLPG sensor probe provides a platform for other applications, such as uranium (VI) absorption from aqueous solutions [7]. Future work will involve functionalizing the GO layer with biomolecules and nanoparticles to develop highly selective and sensitive fiber optic biosensors.

References

1. R. S. Marks, C. R. Lowe, D. C. Cullen, H. H. Weetall, and I. Karube,“Handbook of Biosensors and Biochips,” (Wiley, Weinheim, 2007).
2. F. Esposito, A. Srivastava, L. Sansone, M. Giordano, S. Campopiano, and A. Iadicicco, “Label-Free Biosensors Based on Long Period Fiber Gratings: A Review,” IEEE Sens. J. **21**, 12692-12705, (2021).
3. X. Shu, L. Zhang, I. Bennion, “Sensitivity Characteristics of Long-Period Fiber Gratings,” J. Light. Technol., **20**, 255–266 (2002).
4. J. Peña-Bahamonde, H. N. Nguyen, S.K. Fanourakis et al., “Recent advances in graphene-based biosensor technology with applications in life sciences,” J. Nanobiotechnology, **16**, 75, (2018).
5. Z. Gu et al.,“Dual peak resonance and transmission spectrum characteristics in a coated long-period fiber grating,” J. Opt. A: Pure Appl. Opt., **11**, 085701, (2009).
6. K. P. W. Dissanayake, W. Wu, H. Nguyen et al., “Graphene-Oxide-Coated Long-Period Grating-Based Fiber Optic Sensor for Relative Humidity and External Refractive Index,” J. Light. Technol., **36**, 1145-1151, (2018).
7. P. Yang, Q. Liu, J. Liu et al.,“Resonant THz-meshes,“Bovine Serum Albumin-Coated Graphene Oxide for Effective Adsorption of Uranium(VI) from Aqueous Solutions” Ind. Eng. Chem. Res., **13**, 3588-3598, (2017).