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Extended Abstract

Gold nanogratings on polymers for plasmonic biochemical sensors †

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Abstract: A novel biochemical sensing approach based on a nanoplasmonic sensor chip, realized exploiting a polymer chip combined with a specific biomimetic receptor, has been shown. The plasmonic phenomena are excited and interrogated via two custom experimental configurations, based on polymer optical fibers (POFs) and designed holders. Both setups have been used to measure the disposable gold nanograting (GNG), realized on a PMMA chip, by considering the PMMA chip as a waveguide, in one configuration, or as a transparent substrate, in another configuration. The examined plasmonic sensor configurations here reported have been realized and experimentally tested. To test the biosensing capabilities of the proposed method, as proof of concept, a receptor specific for the bovine serum albumin has been used.

Keywords: nanoplasmonic sensors; plastic optical fibers; e-beam lithography; biochemical sensing.

1. Introduction

Optical fiber surface plasmon resonance (SPR) and localized surface plasmon resonance (LSPR) biochemical sensors play an essential role in many research fields since they are suitable for on-site and real-time monitoring of several analytes in different matrices [1–5]. In order to optimize the performances of these kinds of biosensors, in terms of sensitivity, robustness, and miniaturization, several innovative solutions have been adopted [6–8]. The optical fiber sensors can be defined as intrinsic and extrinsic, according to the interaction of the fiber with the analyzed medium (intrinsic scheme) or its use as a mere waveguide allowing the launch of the light to the sensing region and its collection (extrinsic scheme). Moreover, the sensing scheme may be classified as reflection mode, where the light source and the detector lay on the same side of the fiber, or as transmission mode, where they are on opposite sides.

In this work, we have designed, developed, and tested a plasmonic sensor configuration based on gold nanogratings (GNGs), fabricated by electron-beam lithography (EBL) on the surface of a polymethylmethacrylate (PMMA) substrate and monitored by two custom setups, realized with polymer optical fibers (POFs) and 3D-printed holders [9,10]. In particular, two different kinds of transmission extrinsic optical fiber sensors are presented. In the first case, we have considered the PMMA chip a transparent substrate, whereas in the second one, we have considered it a slab waveguide able to excite the plasmonic phenomena on its surface. To test the biochemical sensing capabilities in both

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experimental configurations, we have functionalized the GNGs surface with a biomimetic receptor specific for bovine serum albumin (BSA).

2. Plasmonic sensor systems

2.1 Sensor chip based on GNG-MIP

The plasmonic GNG sensor has been fabricated how here reported schematically. The sample consists of a PMMA chip, on which is spun about two hundred nanometers thick positive PMMA e-beam resist layer. The nanograting pattern is obtained by an electron beam lithography (EBL) system. After the development process, a 40 nm thick gold film is deposited through a sputter coater machine. All the pattern covers an area of 1 mm^2 at the centre of the PMMA chip [9,10].

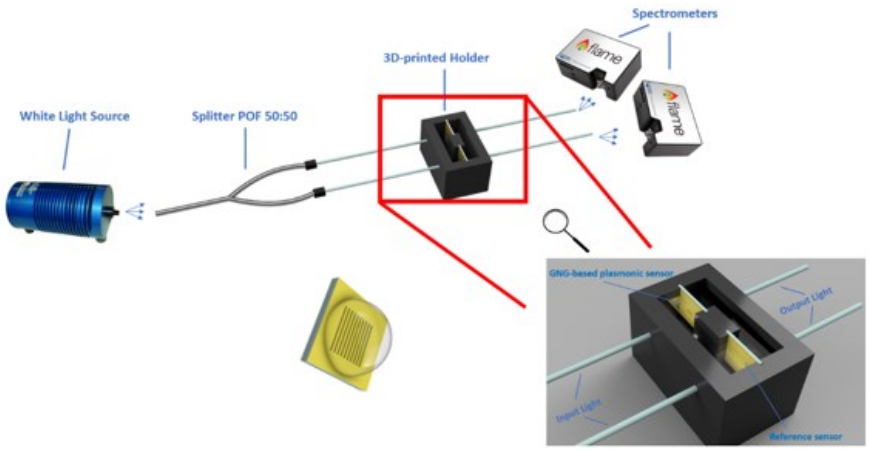
In a second step, the GNG surface has been covered by a Molecularly Imprinted Polymer (MIP) receptor specific for BSA, whose preparation is extensively reported in [9].

2.2 Experimental configurations

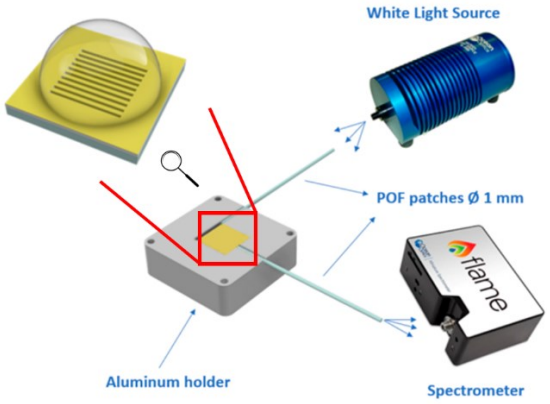
Figure 1 shows both the proposed experimental setups used to test the GNG-MIP sensor chip. In particular, Figure 1a shows the first experimental configuration, where the PMMA chip is used like a transparent substrate. The same setup also reports a reference chip, a PMMA chip with the same gold film but without the nanograting, helpful for the normalization process. As shown in Figure 1a, the 3D-printed holder contains both the chips in an orthogonal position with respect to the transmission light.

On the opposite, in the experimental setup shown in Figure 1b, the plasmonic sensor chip is used as a slab waveguide. It is housed in an aluminum holder with a specific trench, used to enlarge the number of angles to excite plasmons [10].

The equipment used for both the experimental configurations is based on a halogen lamp (HL–2000–LL, Ocean Optics), used as a white light source, and spectrometers (FLAME-S-VIS-NIR-ES, Ocean Optics) connected as reported in Figure 1.



(a)



(b)

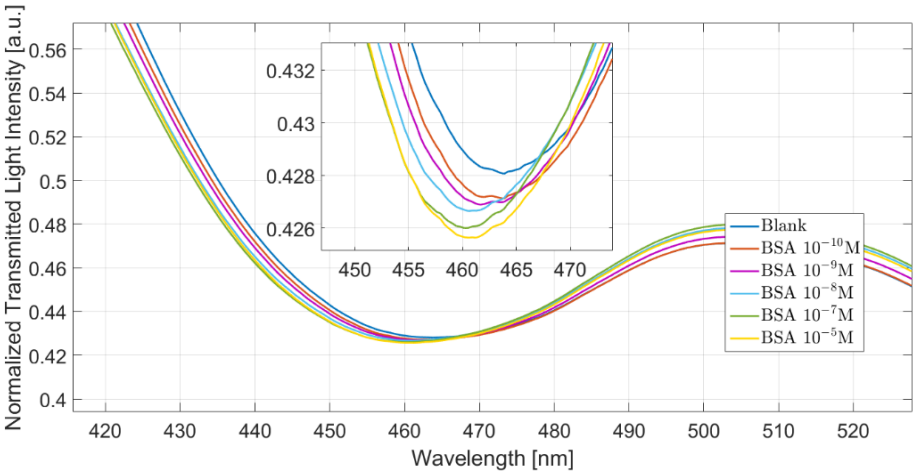
Figure 1. a) Experimental configuration where the PMMA chip is considered as a transparent substrate; b) Experimental configuration where the PMMA chip is considered as a slab waveguide.

3. Experimental results

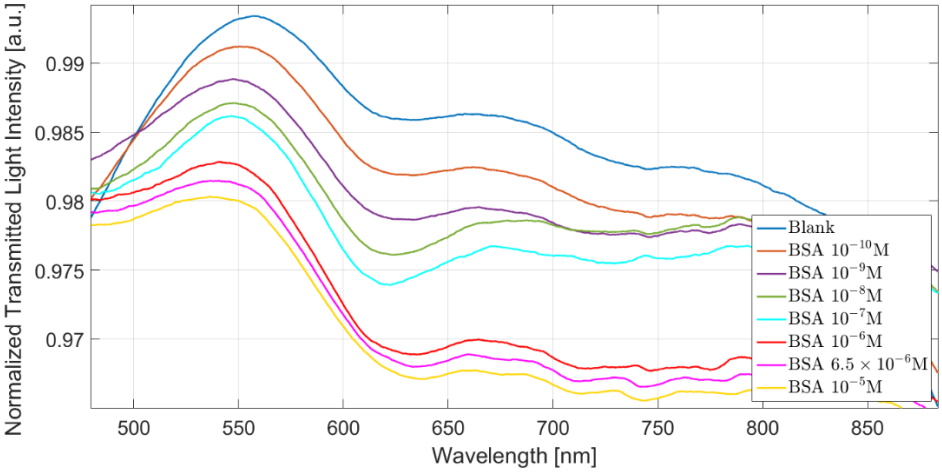
Both the reported experimental configurations have been tested with several BSA concentrations to carry out the binding tests. In particular, Figure 2a shows the plasmonic spectra obtained by the first experimental configuration reported in Figure 1a. Each experimentally measured plasmonic spectra have been obtained by normalizing the transmitted spectra, acquired through the sensor with nanograting, with respect to the reference sensor. As is clear, a blueshift of the resonance wavelength is observed when the analyte concentration increases and this particular behavior is ascribable to the excitation of plasmonic hybrid modes [9].

On the opposite, when considering the second experimental configuration reported in Figure 1b, two distinct plasmonic phenomena can be distinguished (see Figure 2b) when the nanostripes forming the nanograting pattern are located along the same direction of the input light [10]. Each peak (at 550 nm and 630 nm) in the plasmonic spectra presented in Figure 2b is sensible to a different BSA concentration range, as described in [10].

In both the experimental configurations, we have obtained a similar limit of detection (LOD) equal to about 37 pM for the first one and about 23 pM for the second one (with regard to the peak at 550 nm).



(a)



(b)

Figure 2. Plasmonic spectra relative to a) first experimental configuration and b) second experimental configuration.

4. Conclusions

We have reported two BSA sensor configurations, based on a GNG-MIP chip monitored by two setups, showing an ultra-low detection limit (≈pM) in both cases. In addition, one of the experimental solutions has also demonstrated its effectiveness to detect simultaneously also higher BSA concentrations, so widening the detection range.

For these reasons, the reported experimental configurations have shown to be an effective sensing approach solution that could be used in those biochemical applications where higher sensitivity is required together with reduced costs. In fact, the presented nanostructures can be realized through typical microelectronics processes, so leading to economic advantages of large-scale production.

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Conflicts of Interest: The authors declare no conflict of interest.

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