Functionalized Long Period Grating—Plasmonic Fiber Sensor Applied to the Detection of Glyphosate in Water

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***Abstract*—Selectivity was added to a refractometric fiber sensor based on a long-period grating coated with a film of gold nanoparticles by the functionalization with cysteamine. The sensor was applied to the detection of glyphosate in water. Sensor operation is based on the reaction between glyphosate molecules and cysteamine that modifies the effective refractive index of the long-period grating cladding modes. In the presence of water containing glyphosate, spectral changes occur in the long-period grating attenuation bands, allowing the sensor interrogation both in wavelength and intensity. The sensor relies on the high sensitivity of long-period gratings operating at the visible spectral range near the turning point, as well as on the resonance between the cladding modes and the plasmon resonance band of the nanoparticles. It was shown that the resonance between the LPG and LSPR bands increases the sensitivity of the LPG attenuation bands to the glyphosate in the samples. The sensor configuration proposed in this paper was tested with water samples deliberately contaminated with glyphosate showing a limit of detection about 0.02 μM.**

***Index Terms*—Chemical sensor, nanomaterials, nanoparticles functionalization, optical sensor, surface plasmon resonance.**

I. Introduction

PROPERTIES of optical fiber and optical fiber gratings have been used by researchers for sensing applications in many different areas [1]. When sensing a specific parameter, the optical fiber can be used not only for guiding light to/from the sensor but also as the transducer itself. The working principle of fiber optic transducers is based mainly on the spectral modifications occurring in the guided light due to the changes in the measurand. In the particular case of refractometric sensing, the analyte interacts directly with the fiber surface, modifying the guiding conditions and consequently producing detectable spectral changes in the transmitted/reflected light.

In the transducers based on etched fibers and fiber Bragg gratings (FBG), the fiber cladding must be total or partially removed to allow the analyte to interact with the evanescent field of the modes propagating in the fiber core [2]. Despite providing refractive index sensitivity, the fiber integrity is affected, a drawback that cannot be neglected in field sensing applications. An option to avoid the need for etching is the use of specialty fibers such as D-shaped [3], photonic crystal fibers (or holey fibers) [4], [5] and suspended core fibers [6] in chemical sensing. Alternatively, many works have proposed refractometric sensors based on long period gratings (LPG), which couples light propagating in the fiber from the core to the cladding modes [7]. LPG has the advantage of being naturally sensitive to the medium surrounding the fiber with no need for removing the cladding. Optical fibers devices have also been used to excite surface plasmons (whether localized or not) of a metal layer deposited over their surface resulting in refractometric sensors with improved sensitivity [8]–[10]. Besides the experimental work, several works are devoted to the establishment of theoretical models for surface plasmons fiber grating sensors [11]–[14].

Despite the progresses in the field of chemical sensing, sensors that show not only high sensitivity but also some selectivity are required for bio-sensing applications. In this sense, the fiber surface must be covered with an extra layer, which will work as a support for the biomolecular recognition element specific to the analyte of interest. Different approaches have been proposed for the functionalization of the sensor surface aiming for selectivity, as the fiber coating with metallic nanoparticles used as support for the recognition elements. Sensors with improved sensitivity and extended dynamic range can be realized from the excitation of the localized surface plasmon resonance band (LSPR) of the nanoparticles by the light propagating in the fiber [15]–[17]. The electromagnetic field of the incident light produces the collective oscillation of the conduction electrons at the nanoparticle surface responsible by the plasmon resonance band.

Spectral characteristics of the LSPR band are related to the distance among the nanoparticles as well as to their size and shape distributions [18], but are also influenced by the medium surrounding the nanoparticles. These unique optical properties of metallic nanoparticles have been applied for chemical and biological sensing [19]. The majority of the colorimetric techniques are based on changes in the shape and position of the LSPR band. Although these techniques represent a simple approach, they not always have selectivity to distinguish different analytes present in the same sample.

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