

Plasmonic U-Shaped Optical Fiber Sensor for Glyphosate Detection in Water

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Abstract— We show the fabrication and characterization of a plasmonic plastic optical fiber sensor for detection of glyphosate in water. Cysteamine-encapsulated gold nanoparticles produced by the bottom-up method were deposited on the surface of a U-shaped fiber to improve the sensing performance. Within the range up to 50 μM , an average sensitivity of - 0.2 nm/ μM for glyphosate detection in water was determined. This sensitivity relates to a 0.3 μM sensor resolution considering the interrogation system used, which is 10 times smaller than the Brazilian standard for glyphosate in drinking water.

Keywords— Pesticide detection, gold nanoparticles, LSPR

I. INTRODUCTION

Commercialized since 1974, the broad-spectrum herbicide glyphosate (N-(phosphonomethyl)glycine) is the most used active ingredient in agriculture in Brazil. It is applied for selective weed control, mainly in farms of genetically modified seeds of soybean, corn and cotton. The intensive use of glyphosate leads to an accumulation of residues in soil, spreading the contamination by runoff [1] and eventually reaching sources of drinkable water. In order to minimize its hazardous effects for humans and for the environment, the development of fast and portable sensing techniques is required.

Optical fiber sensors fulfill such demand, offering additional advantages as low cost, compatibility with off-the-shelf optical components, real time and even remote monitoring [2]. Combining these characteristics with nanotechnology, localized surface plasmon resonances (LSPR) from metallic nanoparticles is an efficient platform for sensing bio-molecular compounds. Along the last years a number of such plasmonic optical fiber biochemical sensors was described [3]. A U-shaped LSPR probe comprises a bent section of an optical fiber coated with metallic nanoparticles. The geometry is simple to accomplish in plastic optical fibers (POF) and increases the sensor sensitivity. It is also an efficient approach for biological sensing in specific environments [4].

In this work, a U-shaped plastic optical fiber (U-POF) was coated with a layer of gold nanoparticles (AuNPs). A colloidal solution of nanoparticles encapsulated in cysteamine was used to produce the coating on the fiber surface.

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Film deposition was monitored by UV-VIS absorption spectroscopy. Response and calibration curves for glyphosate detection were determined by UV-VIS transmission spectroscopy.

II. EXPERIMENTAL METHODS

A. U-Bent Fiber Probe

Fig. 1 shows a diagram of the U-POF sensor head consisting of a bent portion of fiber 2 cm long produced in a fiber segment 40 cm long. The fiber was inserted in two slits 1.5 cm apart each other engraved on a substrate, in order to produce the curvature that allows the evanescent wave penetration into the external medium. The slits were sealed with a photo-activated dual-curing cement. Then, the bent region was warmed-up to 70 °C for 20 min and annealed to room temperature, resulting in a U-shaped section with radius of 1.5 cm. The bent fiber was immersed in isopropanol for 2 min and rinsed with distilled water. After cleaned, the U-shaped fiber was coated with gold nanoparticles.

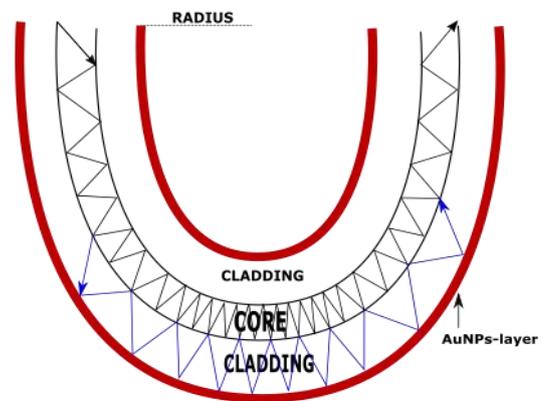


Fig. 1. Diagram of U-shaped structure and light path

For a propagating mode whose ray does not fulfill the total internal reflection condition at core-cladding interface, light propagating in the cladding can give rise to a whispering gallery mode (WGM). When the WGM returns to the core, it interferes with the remaining light according to [5]:

$$I = I_{co} + I_{wis} + 2\sqrt{I_{co} + I_{wis}} \cos\Phi \quad (1)$$

where I_{co} and I_{wis} are the intensities of the core and WGM modes, respectively, and Φ is the phase difference between them.

Beyond the cladding-external medium interface, the amplitude of the evanescent wave decreases exponentially with a skin depth given by:

$$d_p = \frac{\lambda}{2\pi(n_{co}^2 \sin^2 \theta - n_{cl}^2)^{1/2}} \quad (2)$$

where λ is the light wavelength, n_{co} is the core refractive index, n_{cl} is the cladding refractive index and θ is the incident angle at core-cladding interface.

The interaction between the evanescent wave and the external medium affects the intensity of the transmitted light (1) though the U-POF probe, allowing for the sensing.

B. Materials and reagents

The core and cladding of the POF (ESKATM, CK 10, 250 μm diameter) are made of polymethyl methacrylate (PMMA) and a fluorinated polymer, with refractive indexes of 1.49 and 1.41, respectively. Tetrachloroauric acid (HAuCl₄), cysteamine chlorohydrate (HSCH₂CH₂NH₂.HCl) and glyphosate were purchased from Sigma Aldrich. Sodium borohydride (NaBH₄) from ALPHATEC. Deionized water was used in all the experiments.

C. Gold Nanoparticle Synthesis and Film Deposition

For the synthesis, 8.3 μL of HAuCl₄ were stirred together 250 μL of cysteamine (0.213 M) used as stabilizing agent in a beaker containing 25 ml of water at 60 $^\circ\text{C}$. For the reduction, 12.5 μL of NaBH₄ (10 mM) were added, keeping the stirring until the solution acquired a homogeneous red color.

After the synthesis, the U-POF was immersed for 5 min in the colloidal solution of nanoparticles bonded to cysteamine (Cys-AuNPs) allowing the film deposition on the bent region. The coating evolution was monitored by UV-VIS absorption spectroscopy with an optical fiber spectrometer (Ocean Optics, HR4000, 3.3 nm bandwidth), as shown in Fig. 2. After the end of the coating process, the fiber was allowed to dry at room temperature.

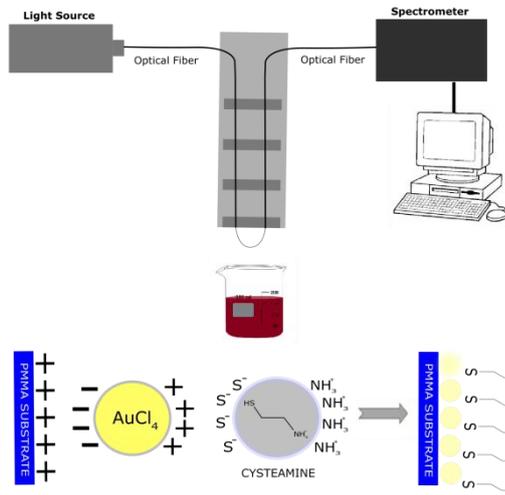


Fig. 2. Schematic diagram for the experimental set-up used in the production of the U-POF LSPR sensor.

D. Sensor Application

Response and calibrations curves of the U-POF LSPR sensor were determined for aqueous samples of glyphosate with concentrations of 1 μM , 4 μM , 10 μM , 20 μM , 50 μM

and 200 μM . All samples presented the same refractive index of (1.3332 ± 0.0004) , measured with an Abbe refractometer (Atago, DR-A1, 0.0005 resolution, 1.3000 – 1.7100 nD) at (19.0 ± 0.2) $^\circ\text{C}$. Transmission spectra measured with a UV-Vis spectrometer (HR4000, Ocean Optics) coupled to a visible light source (LS-1, Ocean Optics) were taken by consecutively immersing the sensor in samples at (19.0 ± 1.0) $^\circ\text{C}$ following an increasing concentration of glyphosate. For the sake of comparison, the same set of measurements was carried out for the sensor without the metallic film deposition.

III. RESULTS AND DISCUSSION

A. Nanoparticle Film Deposition

Absorption spectra acquired during the metallic Cys-AuNPs film deposition (along 5 min) on the fiber surface are shown in Fig. 3. The characteristic Au plasmon resonance close to 550 nm shows a ~ 5.3 nm redshift and an absorption saturation close to 300 s. This behavior was already observed in literature and is associated with the extent of surface coverage by the AuNPs and its effect via electrical interaction on the per-particle surface extinction coefficient [6]. A (551.8 ± 1.0) nm asymptotic value for LSPR peak was found.

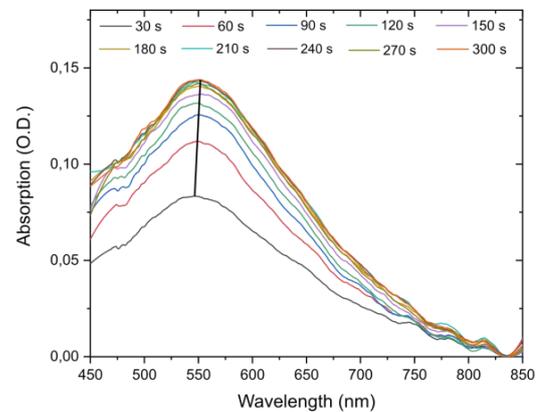


Fig. 3. AuNPs LSPR evolution during the film deposition on the U-POF surface.

B. Glyphosate Sensing

For the sake of comparison, transmission spectra of the U-POF sensor immersed in the water-glyphosate samples before and after the deposition of the metallic AuNPs coating are shown in Fig. 4 and Fig. 5.

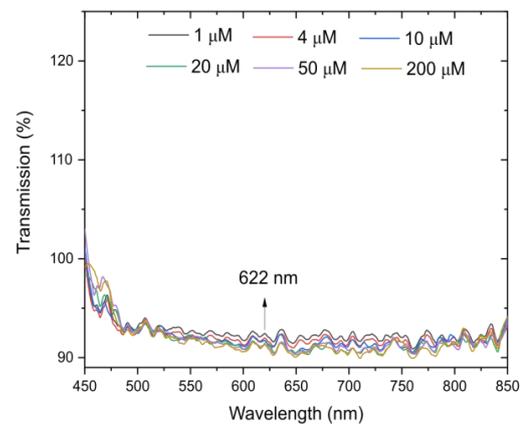


Fig. 4. Transmission spectra of the U-POF sensor without coating for different glyphosate concentrations.

IV. CONCLUSIONS

The proposed U-shaped plastic optical fiber showed the possibility of increasing the sensitivity by coating the fiber surface with a film of Au nanoparticles. The stabilization of AuNPs with cysteamine proved to be effective to allow the bonding with glyphosate molecules. The sensor is an alternative for fast and inexpensive analysis of drinking water regarding the standards for this herbicide.

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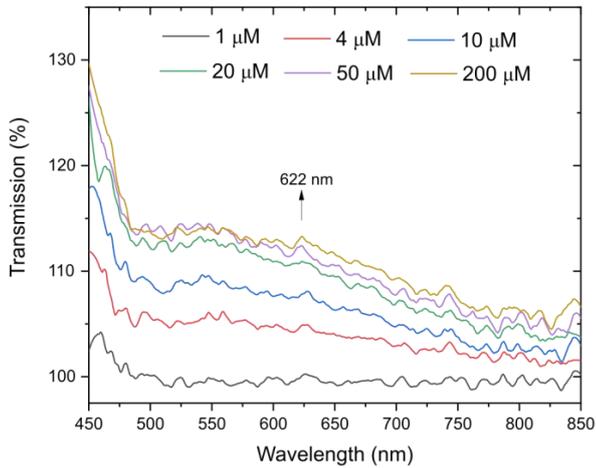


Fig. 5. Transmission spectra of the U-POF with the Cys-AuNPs coating sensor for different glyphosate concentrations.

After the film deposition and the bonding of glyphosate molecules to the Cys-AuNPs, transmission spectra (Fig. 5) changed when compared with the previous configuration (Fig. 4). The same studied band close to 622 nm now shows a blue shift as the glyphosate concentration increases. This shift can be used to quantify the glyphosate in a wavelength-coded approach.

In Fig. 6 is shown the response curve for the experimental points within the concentration range of glyphosate analysed.

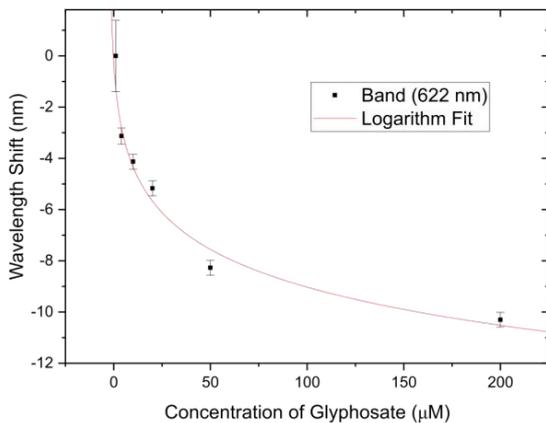


Fig. 6. Response curve of the U-POF LSPR sensor for wavelength-coded sensing.

Error bars stand for the combined standard uncertainty considering the wavelength standard deviation of the mean, the uncertainty in the determination of the band close to 622 nm and the samples concentration error.

For glyphosate concentrations up to 50 μM , an absolute average sensitivity of 0.19 nm/ μM was found, which relates to an approximate 0.3 μM resolution considering a wavelength stability of 0.05 nm for the spectrometer. Taking in account the Brazilian standard for glyphosate in drinking water of 500 $\mu\text{g/L}$ ($\sim 3 \mu\text{M}$), the performance of the proposed sensor is adequate.