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One step method to attach gold nanoparticles onto the surface of an optical fiber used for refractive index sensing

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ABSTRACT

Localized surface plasmon resonance (LSPR) has recently emerged as an efficient and powerful tool for bio-photonic applications due to its high sensitivity to refractive index changes. One technique to excite LSP is by the interaction of the evanescent wave of the light guided by an optical fiber with metallic nanoparticles deposited over the surface of the fiber. This paper proposes a novel, simple, and fast method to attach gold nanoparticles to the optical fiber surface, which can be used to construct highly sensitive refractive index sensors based on localized surface plasmon resonance. A hetero-core structured fiber, composed by a small section of single-mode fiber inserted in a multimode fiber, was coated with nanoparticles using the method proposed here. A sensor sensitivity and resolution of 765 nm/RIU and $\sim 1 \times 10^{-4}$ RIU, respectively, were estimated over a refractive index range of 1.333–1.365. This coating method is appealing to construct optical fiber refractive index sensors since it is very simple and low cost.

1. Introduction

LSPR are charge density oscillations confined to metallic nanoparticles (NPs) and nanostructures [1]. Any change in the refractive index (RI) of the NPs surrounding medium produce a change in the resonant frequency that can be observed as a change in the intensity and/or the central wavelength of the LSPR absorption band [1,2]. Soft solution processing, a controlled precipitation and concurrent stabilization of incipient colloids in aqueous solution at moderate temperatures and pressures [3,4] is traditionally used to prepare metallic NPs. Nanoparticles have to be stabilized to control its shape and size, for example attaching them covalently to a thiol- and disulfide-functionalized monolayer [5,6].

For practical applications, RI sensing, NPs can also stabilize if they are *in-situ* generated and trapped in templates (for example polymers) [7]. In all these cases the NPs are attached in a random fashion, however, for some applications arrayed NPs are necessary. These types of films can be produced by combining methods like vacuum evaporation, electron beam lithography, laser ablation or electro-chemical deposition [8]. These techniques are expensive and cannot be used for massive production. In all cases, the time needed to attach NPs to a desired substrate is quite long; in general, it takes several hours or even days [9].

Practical exploitation of metallic NPs, for instance RI sensing based on LSPR, requires a simple method to couple light to NPs film. In this sense, the evanescent field in optical waveguides is an efficient mechanism that has been successfully used to demonstrate a wide variety of optical sensors for biomedical applications. However, in standard fibers the evanescent field is confined to the core-cladding interface where the effects of the external medium are practically null [10]. In order to extend the evanescent wave to the outer fiber cladding-external medium interface, several methods have been developed; the most common consists of changing the fiber structure by etching, tapering or a combination of both [11]. Unfortunately, these processes could weaken the fiber so it has to be mounted in a rigid structure, in order to keep it safe, which could impose some restrictions to the sensors final structure and applications. In devices like long period fiber gratings, tilted fiber Bragg gratings, or hetero-core structured fibers, where original fiber diameter is not altered, the excitation of fiber cladding modes allows the evanescent field to extend beyond the fiber frontier and interact with external medium [10–15]. The sensitivity of these devices increases when the external refractive index approaches to the refractive index of the cladding [10–15]. In order to enhance the sensitivity of these devices to lower refractive indexes, fiber devices have been coated with nano-layers or nano-particles of noble metals to excite, at a proper light wave-

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length, surface plasmon resonance (SPR) [9] or LSPR [2], respectively. Then, these metalized devices have been coated with thin layers of selective materials that change the optical properties under the presence of a specific chemical compound or biological agent [10].

In a hetero-core structured fiber, which consists of a single mode fiber inserted between two multimode fiber sections, the intensity of the transmitted signal is modulated by external refractive index changes [11]. This behavior has been used to demonstrate a RI sensor [12] and hydrogen leakage sensor (when fiber is coated with a thin film of Pd or Pd–Au) [13]. To increase the RI sensitivity of the device, a thin gold film produced by thermal evaporation was attached to the sensitive section of the hetero-core fiber in order to excite surface plasmons [14,15]. To produce a uniformly thin film around the whole perimeter of the fiber, some authors propose to rotate the fiber during the evaporation process [11,14–19]. However, this technique is complicated, technically impractical and very restrictive. In this sense, the literature reported a LSPR sensor constructed by immobilizing gold nanoparticles (Au NPs) on the surface of hetero-core structures fiber optic and characterized as a refractive index sensor [20,21]. This sensor showed that the propagating loss at 545 nm increased according to increasing of ethanol concentration in water, derived from the refractive index increase of the mixture [17], but they did not observe any shift in the resonance peak. The method to attach the nanoparticles to the fiber comprises several steps and it takes several hours. In this paper we propose a one-step and simple method to coat the fiber with gold nanoparticles as an alternative to increase the sensitivity of hetero-core fiber RI sensor.

2. Material and methods

Metallic nanoparticles are generated and stabilized simultaneously over the fiber section, by immersing the fiber in a solution of 17 μL of $HAuCl_4$ and 33 μL of $NaBH_4$ at a concentration of 10 and 8 mM, respectively. Then the solution was heated by using a heat gun at a temperature of 150 °C over 2 min in order to accelerate the formation of Au NPs while the liquid is evaporated. A portion of the Au NPs generated was attached to the fiber surface. Finally, a triple washing procedure with distilled water and isopropyl alcohol was applied to remove any undesirable residue form the fiber surface.

The fiber was mounted in a mechanical stand where the sensitive section of the hetero-core fiber, SMF section, was inserted in a U-shaped container 10 mm long and 5 mm diameter. We fabricated several samples with this procedure, the Au NPs coated-fibers exhibit the characteristic LSPR peak loss band in the transmitted spectrum (centered at 650 nm). Then the fibers were immersed in different glycerin–water solutions to test their response to refractive index changes.

A sensor sensitivity and resolution of 765 nm/RIU and 1×10^{-4} RIU, respectively, were estimated over a refractive index range of 1.333–1.365. We can assume that in this structure the fiber cladding acts as the core and the external medium as a cladding. The effective index of the excited cladding modes are determined by the cladding and external medium refractive index. Such modes induce evanescent interactions and therefore the transmission of the structured fibers (which can be calculated with the well-known Fresnel coefficients) will depend on the RI of the external medium.

The hetero-core fiber structure first proposed by Watanabés group [11], shown in Fig. 1, has been extensively used in a number of sensor applications since this device combines simplicity, compactness, low cost and high resolution [11–15]. The basic structure consists of a short section of single mode fiber, which works as a sensing element, inserted into a fiber with larger core diameter (single-mode or multimode). The structure used here was constructed with a section of conventional step-index single-mode fiber (Corning SMF-28e) of length L inserted between two graded-index multimode fibers (Corning GI-MMF), whose core diameter was 9 and 62.5 μm, respectively. The outer diameter of the final structures is 125 μm, this could help to keep the mechanical properties of the structured fiber very similar to that of a bare fiber, which makes our device robust and easy to handle. The fabrication process of the structure is very simple and repeatable, since it only requires a high-precision fiber cleaver and a fusion splicing machine; moreover, it takes only a few minutes. The total insertion losses of the process were around 3 dB. In hetero core structures, where a fiber section is inserted between two fibers with bigger core diameter, the fiber section with smaller core diameter works as the sensing region. The core diameter mismatches show that in such a region, light is largely leaked into the cladding region.

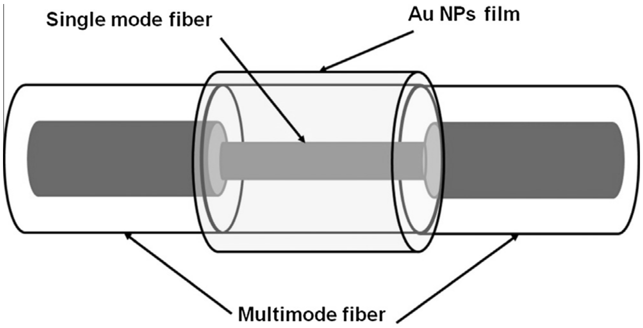

Fig. 1. Representation of the final structure of the optical fiber hetero-core sensor, consisting of a piece of single mode fiber (SMF) of length (L) longitudinally placed between two multimode fibers (MMFs).

The interrogation scheme to measure the transmission characteristics of the hetero-core optical fiber before and after coating is shown in Fig. 2. The hetero-core fiber structure was mounted in a mechanical stand, where the sensitive section was held straight in a testing cell, and the fiber ends were spliced to a pair of FC/PC MM fiber pigtails. This arrangement facilitates the plug in of the fiber to a low-power LED or a white light source and a photodetector or an optical spectrum analyzer (OSA). For the refractive index characterization of the hetero- fiber, before and after coating with Au NPs, we prepared a series of water ($n_D = 1.333$) and glycerin ($n_D = 1.473$) solutions to be used as RI standards, in which the refractive index is determined by the weight percentage of the constituents.

The calculated refractive index of the solutions were verified with an Abbe refractometer. We first fabricate several hetero-core fibers, following the same procedure described in the previous section. Some of these samples were used to test the response of the fiber to refractive index using a low-power LED centered at 850 nm and a power meter (OZ optics). The sensitive section of the fibers was immersed in liquids with different refractive index. All the results obtained were triplicated.

3. Discussion of results

In Fig. 3, we show the normalized transmission of the uncoated hetero-core fiber as a function of the liquid RI. As can be seen in the figure, for refractive index lower than 1.43 the fiber transmission is practically unaltered, i.e. the fiber is insensitive. However, as the external refractive index increases and approaches to that of the cladding, the power of the transmitted light abruptly decreases