Sensors and Actuators B 230 (2016) 536–543

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Development of LSPR based U-bent plastic optical fiber sensors

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ARTICLE INFO

Article history:
Received 26 September 2015
Received in revised form 16 February 2016
Accepted 17 February 2016
Available online 22 February 2016

Keywords:
Evanescent wave absorbance
U-bent plastic optical fiber
Optimum bend diameter
Refractive index
Localized surface plasmon resonance (LSPR)
Plasmonic sensor

ABSTRACT

This study presents design and development of evanescent wave absorbance based U-bent plastic optical fiber (POF) probe with high sensitivity and its applications to refractive index (RI) sensing. The probes were fabricated by a controlled decladding procedure to remove the fluorinated polymer without damaging the poly methyl methacrylate (PMMA) core and a simple and scalable fabrication technique to obtain POF U-bent probes of desired geometry. U-bent probes of fiber diameter from 250 to 1000 μm were fabricated and optimum bend diameter for each fiber diameter was investigated. The sensitivity was found to be maximum when the bend diameter of the probe varies from 2 to 3 times the fiber diameter. Probes with 500 μm core and 1.25 mm bend diameter showed highest sensitivity ($5.57\Delta A_{560\,nm}/\Delta RIU$) in the visible region to RI changes from 1.33 to 1.47 with a resolution better than 1 milli RI units. Furthermore, U-bent probes were amine functionalized and coated with gold nanoparticles to obtain a localized surface plasmon resonance (LSPR) based RI sensor that has an 8-fold improvement in RI sensitivity, hence extending their applicability to plasmonic biosensing.

1. Introduction

Precise identification of changes in material composition could be facilitated through their corresponding changes in refractive index (RI), thus enabling the application of refractometers in industries like food processing, drug discovery, automobile, brewery and clinical diagnosis. Although conventional prism based benchtop bulk refractometers are useful for many of these applications [1]. Optical fiber based RI sensors could be highly preferred for several applications where in-situ, real time monitoring is important. They offer many advantages like remote monitoring, multiplexing and flexibility [2,3]. Sensitive RI sensors could be developed using optical fibers based on evanescent wave interactions with the analyte of interest. The principle of evanescent wave fiber optic RI sensors is based on attenuated total reflection, in which the intensity of light propagating through the fiber changes upon a change in RI of the medium. Evanescent wave (EW) is exposed to the sample medium by means of decladding, tapering or side polishing the optical fiber [4]. The demand for fiber optic RI sensors are growing at a large scale due to their applications in wider areas such as detection of environmental toxin like Microcystin LR [5], assessment of gasoline level in automobile tanks [6], determining the salinity of industrial and natural waters [7], evaluating the quality of frying oils [8] and detection of protein biomarkers [9] for clinical diagnosis.

Recently, POF has gained much attention than the conventional silica fibers due to their ease in machinability and handling, thus enabling them to be a viable alternative for mass production [10,11]. Various POF sensor geometries reported in literature for RI sensing include straight decladded fibers [12], partially polished [13], laterally polished [14], D-shaped [15], cuvetted with inline submillimeter hole [16], biconically tapered [17], microbent [18], bent with structural imperfections [19], coiled POF [20] and U-bent [21]. Amongst the various designs reported, U-bent probe has several advantages such as (1) high EW absorbance sensitivity due to conversion of the lower order modes into higher order modes (2) less fragile than other geometries (3) ease in probe fabrication and repeatability (4) can be developed into a point sensor. Subsequently, by combining the advantages of both U-bent geometry and POF, a highly robust and machinable sensor could be designed and fabricated. In addition, POF requires only low temperature processes for bending compared to silica.

So far, POF based U-bent fiber optic RI sensors have been explored using 500 and 1000 μm fibers with a bend diameter that is 5–10 times the fiber diameter and subsequent side-polishing and tapering for further enhancement in sensitivity respectively [21,22]. Our previous studies on optimal probe design show that the bend diameter of a U-bent probe is a critical parameter to achieve efficient mode conversion [23,24]. The choice of the fiber diameter is determined by the applications of interest, ranging from simple

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http://dx.doi.org/10.1016/j.snb.2016.02.074

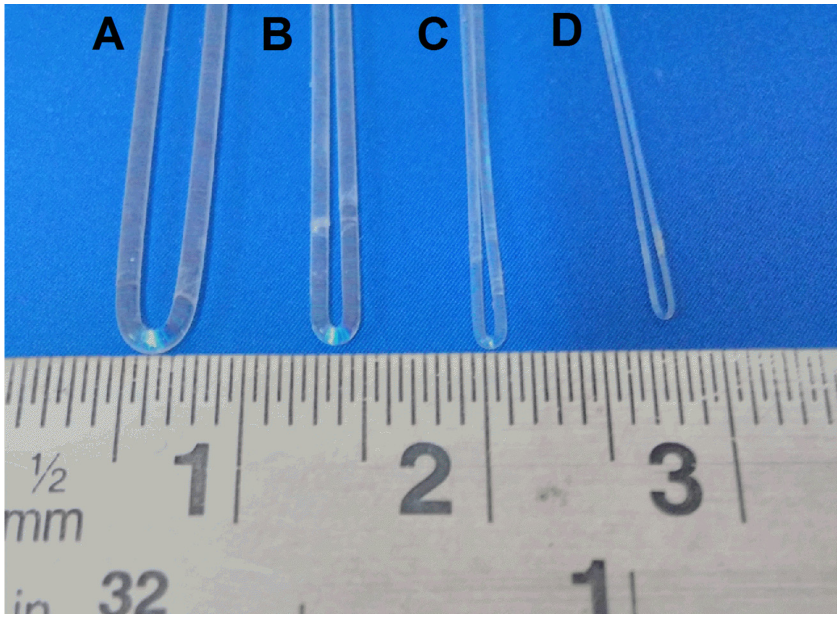

Fig 1. U-bent POF probes (A) 1000 μm with $D = 3$ mm (B) 750 μm with $D = 1.25$ mm (C) 500 μm with $D = 1.25$ mm (D) 250 μm with $D = 0.75$ mm.

chemical to sensitive biomolecular analyses, where smaller diameter fibers (e.g., 250 μm) may offer better response due to improved evanescent wave interactions within smaller active sensing region. These probes could be more efficiently designed and fabricated to obtain much higher RI sensitivity.

In addition, RI sensitivity of the probes could be improved by an order of magnitude with the help of noble metal nanoparticles by virtue of localized surface plasmon resonance (LSPR) phenomenon [24]. Due to LSPR, the metal nanoparticles (gold and silver) exhibit a strong absorption band in visible region of the spectrum that is highly influenced by the size, shape, and local environment of the nanoparticle [25]. U-bent probes having high EW absorbance sensitivity could be utilized to efficiently monitor the changes in the optical absorbance properties of the nanoparticles when bound to the fiber surface.

This study shows a simple method for fabrication of U-bent POF probes with optimum geometry for development of evanescent wave absorbance based RI sensor with improved sensitivity. We have systematically prepared various U-bent POF probes with fiber diameters varying from 250 to 1000 μm having different bend diameters varying from 2 to 10 times the fiber diameter. The procedures for fiber decladding and functionalization of the probes were studied and refined with the help of microscopy and tensiometry characterization tools respectively. Absorbance sensitivity of these probes for varying RI was evaluated to obtain the optimum probe geometry with highest RI sensitivity. In addition, gold nanoparticles (AuNP) were chemisorbed to amine-functionalized U-bent probes to demonstrate LSPR based RI sensor.

Table 1
Details of various U-bent probe geometries fabricated with the glass capillaries.

d[a]	Fiber diameter (Ø, μm)							
	250		500		750		1000	
	ID[a]	D[a]	ID[a]	D[a]	ID[a]	D[a]	ID[a]	D[a]
0.5	1	0.75	1.5	1	2	1.25	2.5	1.5
1	1.5	1.25	2	1.5	2.5	1.75	3	2
2	2.5	2.25	3	2.5	3.5	2.75	4	3
3	3.5	3.25	4	3.5	4.5	3.75	5	4

[a] d, space between the parallel legs of the fiber; ID, inner diameter of the capillary; and D, bend diameter of the U-bent probes respectively; all dimensions are in mm.

2. Materials and methods

The plastic optical fibers (SK10, 20, 30, 40) were provided by Mitsubishi Rayon Co., Ltd. All chemicals including Ethyl acetate, Hexamethylene diamine, Sucrose, $HAuCl_4$ and HEPES procured from Merck, India were of analytical grade. A green LED (IF-E93, i-fiber optics Inc., USA) was used as light source. A fiber optic spectrometer (USB 4000 XR1 ES, Ocean Optics Inc., USA) was used to record the absorbance spectra. The optical power meter (PM100USB) used to measure light attenuation was purchased from Thorlabs Inc., USA.

2.1. Sensor fabrication

POF comprises of polymethylmethacrylate (PMMA) and fluorinated polymer as core and cladding having refractive indices of 1.49 and 1.41 respectively. The POF of 25 cm length was taken and kept inside a glass capillary in hot air oven at 100 °C for 10 min to eliminate the stresses induced in the fiber due to packaging. The fiber was bent in order to bring both ends closer and pushed inside a 15 cm long glass capillary tube of varying inner diameter. The capillary tube was placed in a hot air oven for 10 min at ∼100 °C. Here, fibers are bent by placing them in the hot ambience without subjecting them to a blow of hot air directly [26]. This procedure minimizes the thermal residual stresses and non-uniformity in geometry of the U-bent probe.

2.2. Sensor surface preparation

The U-bent probes were prepared by precisely decladding the fluorinated polymer layer over the U-bent region by chemical etching to sensitize the core surface for evanescent wave based sensing. These probes were decladded by dipping in a vertical flow cell of smaller cross sectional area which was completely filled with ethyl acetate for 2 min. This helps in etching the U-bent region alone leaving the remaining portion of the fiber.