

Controlled chemical modification of the internal surface of photonic crystal fibers for application as biosensitive elements



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ABSTRACT

Photonic crystal fibers (PCF) are one of the most promising materials for creation of constructive elements for bio-, drug and contaminant sensing based on unique optical properties of the PCF as effective nanosized optical signal collectors. In order to provide efficient and controllable binding of biomolecules, the internal surface of glass hollow core photonic crystal fibers (HC-PCF) has been chemically modified with silanol groups and functionalized with (3-aminopropyl) triethoxysilane (APTES). The shift of local maxima in the HC-PCF transmission spectrum has been selected as a signal for estimating the amount of silanol groups on the HC-PCF inner surface. The relationship between amount of silanol groups on the HC-PCF inner surface and efficiency of following APTES functionalization has been evaluated. Covalent binding of horseradish peroxidase (chosen as a model protein) on functionalized PCF inner surface has been performed successively, thus verifying the possibility of creating a biosensitive element.

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1. Introduction

Micro- and nanostructured optical fibers which can emit, modulate and amplify electromagnetic radiation serve as very promising tools in fabrication of high-throughput sensor devices used in biological and medical applications. Photonic crystal fibers (PCF) are a special class of microstructured optical fibers which contains channels and holes in the cladding and/or core [1–3]. PCF are unique since they enable extremely low-loss light transmission because of the photonic band gap effect. PCFs light-guiding mechanism is fundamentally different from that of conventional optical fibers since it is caused by a regular pattern of holes running along the length of the fiber rather than variations in the fiber's refractive index. Moreover, PCFs, especially those with hollow core,

can have theoretically zero dispersion of propagating optical signal that allows the signal transmission with virtually no distortion. These properties make PCFs an object of extensive studies focused towards their application in telecommunications and laser technologies [4].

PCFs optical properties also are widely used in sensors construction [5–7]. PCF sensors are based either on hypersensitivity of their optical properties to the variation of the refractive index of medium filling the PCFs cavities, or on measuring analytical signal (SERS, luminescence, SPR, etc.) of the medium placed into PCFs which serve as an effective signal collector and microfluidic reactor [8–12].

The hollow core photonic crystal fibers (HC-PCF) show much potential as sensitive elements of sensors or tests and possess the ability to quantify analyte concentrations as low as 10^{-10} M using only nanoliter sample volumes [11]. Channels of HC-PCF can be filled with sample and reagents and the presence of foreign molecules and ions causes significant changes in the PCFs optical properties [13]. However, in order to increase selectivity of analysis, chemical functionalization of PCF inner cores surface is preferable. This is particularly important for biomolecule-based methods, e.g.

Abbreviations: PCF, photonic crystal fibers; HC-PCF, hollow core photonic crystal fibers; APTES, (3-aminopropyl)triethoxysilane; GA, glutaraldehyde; HRP, horseradish peroxidase; PBS, phosphate buffered saline; TGA, thermogravimetric analysis.

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immunoassay: sensitivity of heterogeneous methods is usually higher than that of homogeneous methods due to pre-concentration of reagents on the solid surface as well as separation of bound and unbound reagent fractions.

To the best of our knowledge there are only few examples of PCF application as a solid support and a waveguide for biomolecules attachment. Functionalization of PCF inner surface by poly-L-lysine and following covalent bonding of biotinylated DNA oligonucleotide allowed specific detection of fluorophore-labeled biomolecules [14]. Model immunoassay experiment was carried out by He et al. [15] and possibility of monitoring each step of multiple modification and binding was observed. Surface modification included consecutive adsorption of poly(allylamine hydrochloride) monolayer and immobilization of monoclonal primary antibody of anti-rat bone sialoprotein. The immobilization and fluorescent detection of a Cy5-labeled DNA probe in a polyethylene glycol diacrylate hydrogel platform formed within a glass HC-PCF was presented by Ref. [16].

In practice all methods of silicate materials functionalization used to create sensitive elements involve hydroxyl groups at the silica surface (silanol groups). Concentration, type and distribution of surface silanol groups and presence of siloxane bridges define chemical activity and hydrophilicity of the surface. The topology and structure of silicate surfaces formed through the treatment with various inorganic acids has been studied in Ref. [17]. As a result, the hydroxylation of the silica surface is critically important for good performance of any chemical modification of PCF surface. Therefore, it is necessary to develop simple, reproducible and inexpensive methods to control the formation of a layer of silanol groups at the PCF inner surface.

Although chemistry of silicate materials has been an object of intensive studying for decades, there are few approaches for comparatively simple estimation of the number of silanol groups at silica surface, especially in the case of microstructured systems such as PCF. There are some chemical and physical methods for quantitation of surface silanol groups. Most of them are based on the analysis of the products of chemical modification of silanol groups. Determination of number of surface silanol groups has been performed with such agents as dimethylchlorosilane [18], methylolithium [19], lithium aluminum dibutylamide [20] and organosilanes [21]. These chemicals are very toxic, thus requiring a careful control of the reaction conditions.

Physical methods, such as infrared spectrometry and thermogravimetry, have also been used for surface silanol groups study [22]. The determination of surface silanol groups can be performing by tracing the OH stretching vibrations of the free surface silanol groups at 3745 cm^{-1} , the intraglobular silanol groups at 3650 cm^{-1} , the silanol groups hydrogen bonded to water molecules at 3520 cm^{-1} , and the adsorbed water molecules involved in hydrogen bonding at 3400 cm^{-1} . All of the aforementioned bands are broad and overlapping which makes quantitative determination of surface silanol groups rather difficult, particularly for materials with transmission highly dependent on the wavelength.

Significant results have been obtained for mass spectrometric analysis of the reaction products after deuterium exchange [23,24]. Isotopic exchange reactions affect only the surface silanol groups and provide a way to their determination by substituting the hydrogen from surface silanol groups with deuterium oxide and further analysing the isotopic composition of the vapor phase (after the water is converted to D_2 , H_2 and HD) at equilibrium by mass spectrometry. All of the above mentioned methods are time-consuming and expensive, thus inhibiting their application as methods of quantification of silanol groups in PCF.

The aims of this study are to provide an express method of estimation of the amount of silanol groups at the HC-PCF inner

surface; to modify PCF and demonstrate possibility for application of modified PCF as biosensitive elements.

Evaluation of the number of silanol groups during the process of hydroxylation is based on the analysis of the local maximum shift in the HC-PCF transmission spectrum that results from hypersensitivity of such spectra to slight changes in the refractive index of its constituent elements. The relationship between the number of silanol groups on the HC-PCF inner surface and efficiency of the following functionalization with alkoxyxilanes has been studied. The covalent binding of horseradish peroxidase to obtained functionalized surface has been evaluated.

2. Experiment section

2.1. Chemical and reagents

(3-aminopropyl)triethoxysilane (APTES), glutaraldehyde (GA) and horseradish peroxidase (HRP, 250 U/mg) have been purchased from Sigma-Aldrich. Colorburst™ Blue TMB/Peroxide (ALerCHEK, Inc., USA) has been used as substrate chromogenic solution for the HRP-enzyme. Analytical grade reagents and solvents including doubly distilled water have been used throughout.

Stock HRP solution (250 U/mL) has been prepared in phosphate buffered saline (10.0 mM, pH 7.4 (PBS)). Working standard solutions of HRP have been freshly prepared by dissolving the stock solution in PBS.

2.2. Photonic crystal fibers

The samples of chirped-cladding HC-PCF consisting of five concentric layers with the diameter of the hollow core being $284\text{ }\mu\text{m}$ and the outer diameter being 1 mm (Fig. 1) have been used. The HC-PCF manufacturing is based on micro- and nanocapillary glass technology [25].

2.3. Instruments

Pre-treatment of internal surface of HC-PCF has been carried out in a flow-through mode using the Longer Pump BT 100-1F dispensing peristaltic pump (China). Samples are dried in argon atmosphere and kept sealed in order to prevent contamination and wetting.

The transmission spectra, passed through the air-filled 70-mm-long HC-PCF samples, have been studied with the Ocean Optics HR4000 analyzer with Ocean Optics HL-2000-HP used as a source of white light. The final spectra have been calculated as a ratio of

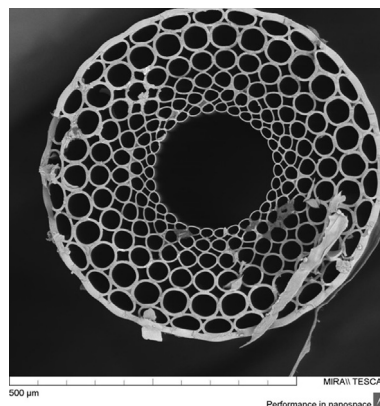


Fig. 1. The cross-section of chirped-cladding hollow core photonic crystal fiber.

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