Layer-by-layer assembled-composite nanocoating for functionalization of microstructured optical fibers

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Abstract. Hollow-core microstructured optical fibers (MOFs) possess the great potential for the integration of different materials inside the holey-capillaries leading to the creation of tailored hybrid structures. Moreover, the further improvement of MOF-based sensor performance can be achieved by exploiting the wide range of post-processing techniques directing to both the enhancement of the existing characteristics and the enabling of new functionalities. Here, we concentrate on hybrid MOFs whose hollow-capillaries were coated through the layer-by-layer assembly technique by a combination of oppositely charged polyelectrolytes and magnetite nanoparticles. We characterize the optical transmission and the fiber loss of the modified samples and show the scanning electron microscopy images illustrating the formed coatings on the inner fiber surfaces.

1. Introduction

The current trend in the development of optical fiber-based sensors is the creation of custom-made structures, combining high detection sensitivity and simple design, for any specific application in spectroscopy, refractometry, and biorecognition [1]. Among the different types of optical fibers, utilized for the creation of sensitive elements, the special class of hollow-core microstructured optical fibers (MOFs) has been extensively elaborated incorporating all the benefits of conventional step-index fibers in addition to their unique properties [2]. The infiltration of liquid samples and the injecting of solid materials inside the air-capillaries of MOFs opens the novel horizons for the application of in-fiber MOF-based sensors which could not be previously realized with the all-solid silica fibers [3,4].

The central light-guiding hollow-core is surrounded by an array of air- or holey-capillaries at different diameters. They serve as periodic cladding layers enabling the light guidance by the coherent Bragg scattering from the glass-air interface [5]. This prevents the light at specific wavelength bands from escaping the hollow-core and allows the guidance over the whole fiber length [6]. Following this model, the condition corresponding to the maxima in the fiber transmission spectrum can be written as follows [5]:

\[ \lambda_j = \frac{4n_1}{2j+1} \left( \frac{n_2^2}{n_1^2} - 1 \right)^{1/2}, \]  

(1)
where \( j \) is an integer describing mode order (\( j = 1, 2, 3, \ldots \)), \( n_1 \) is the refractive index of the medium filling the air-capillaries, \( n_2 \) is the refractive index of the fiber-glass and \( d \) states for the wall thickness of the first capillary layer.

Therefore, the conditions for the light confinement in the central hollow-core may be controlled through the proper choice of the fiber geometry (\( d \)) or by the variation of the optical dispersion of the glass material (\( n_2 \)). Any infiltration or injection of the host materials inside the hollow-core region allows them to be probed by the guiding light and can be detected through the transmission spectra measurements (eq.1).

Here, we have investigated the layer-by-layer (LBL) assembly technique for the consistent modification of the fiber capillaries with a combination of oppositely charged polyelectrolytes and magnetite nanoparticles (Fe\(_2\)O\(_3\)). In our previous paper \([7]\), the fabrication of MOF-based endoscopic probe visible in magnetic resonance imaging was demonstrated through the deposition of the composite nanocoating on the fiber capillaries. In this work, we have further studied the influence of the composite nanocoating on the transmission characteristics of MOFs and investigated the shift of the central wavelength band as a function of the number of deposited bilayers. We have also measured the optical losses of the modified fibers and performed the scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) analysis which prove the formation of the composite nano-coating on the inner surface of the hollow-core.

2. Materials and methods

2.1. MOF samples
The spectral properties of hollow-core MOF used in the experiments are described in detail in \([5,7,8]\). The overall structure consists of periodic concentric air-filled capillaries fabricated from the custom-made soft glass that surrounds the central hollow-core.

2.2. Chemical reagents
The concentrated solutions (2 mg/ml) of polyelectrolytes (PEs, poly(allylaminehydrochloride) (PAH) (MW = 50,000) and polyethylenimine (PEI) (MW = 2,000,000), were prepared in aqueous 0.15 M NaCl solution and together with a hydrosol of magnetite nanoparticles (MNPs) were used for the coating formation.

2.3. Layer-by-layer assembly of composite nanocoating
We have modified the procedure of the capillaries functionalization described in \([7]\) and substituted the pipette dispenser by the automated peristaltic pump. The step-by-step guidance of the deposition process can be found in \([8]\). Briefly, using a combination of oppositely charged PEs and MNPs, we have prepared a set of modified MOF samples with an increasing number of PAH/MNPs bilayers. The very first bilayer consisted of PIE and MNPs.

3. Results and discussion

3.1. Scanning electron microscopy images of modified MOF samples
To prove the fiber functionalization by composite nano-coating, we performed the scanning electron microscopy (SEM) analysis of MOF samples modified with 13 and 28 PAH/MNPs bilayers. From SEM images of MOF cross-sections focusing on the inner surface of the hollow-core, one can observe the clear formation of the nanocoating resulted from the deposition of PEs and MNPs (Figure 1).
From SEM images, the structure and the thickness of the deposited composite coating can be observed (Figure 1). The average thickness of the coating formed by the deposition of 13 PAH/MNPs bilayers is equal to 85 nm and the one for the sample modified with 28 PAH/MNPs bilayer is 216 nm.

The EDX study of the fiber composition shows the increase of Ferrum content with a number of deposited magnetite (Fe$_2$O$_3$) layers that also proves the coating formation (Table 1).

### Table 1. EDX study of fiber composition. The comparison of non-modified fiber with the samples modified with 13 PAH/MNPs bilayers and 28 PAH/MNPs bilayers.

| MOF sample     | Ferrum content in % | Ferrum content in % |
|----------------|---------------------|---------------------|
|                | weighted percentages | atomic percentages  |
| Non-modified   | 0                   | 0                   |
| 13 PAH/MNPs    | 12.22               | 6.14                |
| 28 PAH/MNPs    | 24.08               | 13.01               |

#### 3.2. Optical characterization of modified MOF samples

To characterize the optical transmission of modified MOF samples, we exploited a simple setup consisted of a white light source, a set of focusing and collimating objectives, fibers holders and CCD-spectrometer [8]. The resulted shift of the wavelengths bands in the transmission spectra of modified samples illustrates the formation of the composite coating. The deposition of PEs and MNPs effectively increases the thickness of the first capillary wall ($d$ in eq.1) that leads to the red-shift of the maxima of transmission spectra [5]. To further study the effect of deposited composite nano-coating on MOFs transmission, the set of MOF samples modified with different number of PAH/MNPs bilayers was investigated on optical setup and the position of maxima located near 550 nm was tracked (Figure 2).
Figure 2. (a) Comparison on transmission spectra of non-modified and modified MOFs. (b) The spectral shift of the maximum transmission spectrum located at 550 nm induced by the deposition of composite nano-coating on the inner surface of MOF hollow-core. The dashed line shows the linear fit of the experimental points. The error bars correspond to the spectrometer optical resolution.

3.3. Fiber loss
The additional fiber losses induced by the formed composite nano-coating were estimated using the cut-back technique consisted of a series of three consistent cut-back steps performed on an initial 6 cm long MOF samples (Figure 3).

Figure 3. (a) Fiber loss of non-modified (empty) MOF sample. (b,c) The loss estimation of MOF samples modified with (b) 11 and (c) 23 PAH/MNPs (Fe₂O₃).
The cut-back measurements of MOF samples modified with 11 and 23 PAH/MNPs bilayers enable the estimation of the fiber losses originated from the additional light scattering from the rough composite nano-coating. If 11 PAH/MNPs bilayers do not introduce the significant losses but attenuate the transmission in about 20 dB per meter comparing to the non-modified fiber. This can potentially promote the usage of functionalized MOFs in the extended wavelength range where the glass absorption does not prevent light guidance. In particular, the nonlinear optical experiments utilizing the pulsed femtosecond and picosecond laser sources can be an interesting task. However, further modification and the deposition of the other PEs and MNPs bilayers introduce the high losses and the total attenuation of the transmission wavelengths bands reach 140 dB/m (Figure 3c).

4. Conclusion
In this work, we have further investigated the potential for the usage of layer-by-layer assembly technique to functionalize hollow-core MOFs. We demonstrated the consistent modification of the hollow-capillaries with a combination of oppositely charged polyelectrolytes and magnetite nanoparticles. The additional investigation of the composite nanocoating influence on the optical characteristics of modified MOFs was performed elaborating the transmission spectra measurements. The dependence of the spectral shift as a function of the deposited PAH/MNPs bilayers shows an almost linear increase. The SEM images and EDX analysis also prove the composite coating formation on the inner surface of the hollow-core. Our findings can be used for the further study of an application of layer-by-layer assembly method for the modification of the hollow-core fibers with different functionalized coatings and particles.

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