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ABSTRACT

We report results on the development of an optical fiber long period grating sensor for organic vapor monitoring. A silk fibroin overlayer with a thickness of the order of 400 nm is drop casted on the fiber cladding surface to enable sensing of volatile organic compound vapors. For increasing methanol vapor pressure up to 100 mbar the wavelength of the long period grating attenuation band exhibits a negative shift up to a maximum value of 4 nm. The strength of the grating attenuation band is also altered reaching a 0.27 dB strength decrease under the same maximum methanol vapor pressure. Furthermore, the recovery behavior of the sensor is presented and preliminary results of the response of the sensor to isopropanol and ethanol vapors are briefly discussed.

Keywords: Optical fiber sensors, optical fiber long period gratings, silk fibroin, volatile organic compounds sensor, methanol sensor

1. INTRODUCTION

Silk a natural, insect spun fiber has been used for centuries in the high-end textile industry, due to its distinctive weaving and texture characteristics1. Silk fibroin is a biopolymer extracted through an all-aqueous process, it possesses excellent optical and mechanical properties and it can be relatively easily, chemically and biologically functionalized. Recently, the material properties of Bombyx mori silk fibroin, -the protein extracted from silk fiber- have prompted investigations for the development of biocompatible optical devices. Examples of silk fibroin enabled optical components include microscale optical waveguides that undergo photoactivation2, doped silk diffraction gratings for gas sensing3 and functionalized optofluidic devices4. In the area of optical fiber sensors, the use of silk fibroin can lead to the development of advanced biofunctional sensing devices that combine the advantages of optical fibers and the facile and versatile processability of silk fibroin. Indicatively, silk fibroin has been formed as a thin diaphragm for the development of a fiber-tip Fabry-Perot pressure sensor5. Other recent reports on the development of natural silk-based optical fiber devices include the work of Liu et al. on a humidity detection technique for spectral tuning of whispering gallery modes in a cylindrical microresonator formed by a piece of spider egg sac silk6, while Hey Tow et al. developed an optical fiber using dragline spider silk also for humidity sensing7.

Herein, we report the use of silk fibroin as a sensing outcladding overlayer for the development of an optical fiber sensor for organic vapor monitoring. Alcohols, e.g. methanol, ethanol are basic solvents used widely in chemical, fuel and pharmaceutical industries. Human exposure to methanol vapors can affect the central nervous system and induce medical conditions of escalating severity depending upon the level of exposure. In this context, safety imposes the need for the development of accurate and reliable alcohol vapor sensors, based on non-toxic transduction materials, while being suitable for waving into fabrics, towards wearable device, according the lab-in-a-fiber approach8.

The sensor reported here consists of a thin layer of silk fibroin formed through drop casting onto an optical fiber long period grating (LPG). The response of the sensor is studied in the presence of methanol vapors and discussed in terms of its sensitivity, and response/recovery characteristics. The advantage of the present sensing scheme lies in the use of a

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biocompatible material that combined with the nontoxic and biochemically inert silica fibers can lead to the development of human safe photonic sensing probes.

2. EXPERIMENTAL

For the development of the sensor, long period gratings of 520 µm period and 25 mm length were inscribed in Boron-doped germanosilicate fiber (PS1250/1500–Fibercore Ltd) utilizing a Spectra Physik KrF excimer laser and a titanium amplitude. The laser beam had 34 ns pulse duration and the fluence incident on the fiber was 210 mJ/cm² per pulse, at a repetition rate of 5 pulses/s. Under the above grating inscription conditions LPGs with attenuation bands observable in the 1400-1600 nm region, of up to 15 dB strength, were fabricated for an exposure time of approximately 180 seconds.

Silk Fibroin batches were prepared upon extraction from row Bombyx Mori cocoons following the original Rochwood’s protocol. According to this method, cocoons were first cut in small pieces, using titanium scissors, and afterward boiled in a 0.02 N sodium carbonate (Alfa Aesar) solution for 30 min in order to remove the glue-like cladding made of sericin. Degummed fibroin obtained upon separation from sericin was then washed twice, under gentle stirring conditions, in highly pure water for 20 min aiming at removing eventual sericin excess and were then left to dry under a fume hood overnight.

Degummed fibroin was hence dissolved in 9.3 M lithium bromide (Alfa Aesar) solution for 4 h in a conventional oven at 60 ºC. A slightly amber-like solution without any trace of undissolved fibroin was achieved by the above process. After cooling down, the solution was dialyzed for 48 h in a dialyzer cassette (Slide-A-Lazer 3.5 KDa) against ultra-pure water to remove salts. Water was changed six times during the dialysis process. After dialysis, the SF aqueous solution was centrifuged at 9000 rpm for 20 min at 4 ºC to remove the unsolved portion of fibroin and the procedure was reproduced twice. The obtained solution was stored at 4 ºC to prevent protein denaturation provoking the solution jellification. Aqueous solution of silk fibroin (8% in weight) was drop casted on the optical fiber at the location of the LPG using a hypodermic syringe, by means of a small fibroin droplet.

The response of the sensor in the presence of Volatile Organic Compound (VOC) vapors was tested using a specially designed stainless-steel chamber of ~500 ml volume (Fig.1). Fit-through connectors allowed positioning of the LPG sensor into the chamber while VOCs solvents were injected in liquid form through a dedicated inlet. The chamber was also equipped with a sensitive manometer to record changes in pressure due to the evaporation of the solvent. The sensor characterization measurements were performed using a super-luminescent source and an Optical Spectrum Analyzer (OSA) for monitoring in real time the spectral response of the LPG.

![Figure 1. Stainless-steel chamber for studying the response of the sensor in organic vapor atmosphere](image-url)
3. RESULTS AND DISCUSSION

For the realization and optimization of the sensing probe, the effect of the silk fibroin overlayer formation on the spectral characteristics of the LPG was monitored on situ. For two consecutive passes of the silk fibroin water droplet, the spectra of the main attenuation band before and after applying the overlayer are depicted in Fig. 2. As shown, the change in the strength and wavelength of the main attenuation band are a 2.4 nm blue shift and a 10.5 dB strength decrease, respectively.

![Figure 2. Spectra of the LPG main attenuation band before and after drop casting of the silk fibroin overlayer](image)

Scanning electron microscopy studies of the optical fiber fibroin overlayer revealed a mean thickness value of the order of 400 nm with non-uniformities attributed to the drop casting method and the hydrophobicity of the silicate glass surface (Fig. 3).

![Figure 3. Scanning Electron Microscopy images of an optical fiber with silk fibroin overlayer](image)

To examine the effect of methanol vapors on the response of the sensor, 200 µl of methanol were injected in the chamber of Fig. 1. The transmission signal of the LPG was recorded for increasing methanol vapor pressure up to saturated vapor atmosphere in the chamber. The time interval required to reach a constant methanol pressure in the chamber was of the order of 25-30 min. The sensor response in terms of LPG attenuation band spectral changes is depicted in Fig. 4. For increasing methanol vapor pressure a clear shift towards lower wavelengths and decrease in the strength of the main LPG attenuation band can be seen.
The recorded wavelength shift and notch strength change, versus the methanol vapor pressure in the chamber, are plotted in Fig. 5a and 5b respectively. Results indicate a rapid decrease in the wavelength of the LPG attenuation band reaching a value close to 4 nm for a maximum vapor pressure of 100 mbar, however without reaching saturation for the range of methanol pressure examined. To allow an estimation of the sensitivity of the sensor to methanol vapors, a linear approximation is assumed in the range 80 to 100 mbar while yielding a value of 0.22 nm/mbar. A similar trend was recorded for the strength of the LPG reaching a 0.27 dB strength decrease under the same maximum methanol vapor pressure. The change in the wavelength and strength of the attenuation band of the LPG could be attributed to the binding of methanol to the fibroin protein and resulting changes in its intermolecular H-bonds. 

Upon opening the chamber and re-exposing the sensor to ambient air, the sensor wavelength and strength return to their original values, albeit with a time delay as shown in Fig. 6. Specifically, the wavelength shift recorded immediately after opening of the chamber retains 20% of the methanol induced wavelength shift, while this value drops close to zero approximately after 5 min. An indicative value of the response time of the sensor based on the results of Fig. 6 is ~5 min for the specific silk fibroin overlayer thickness and the examined methanol vapor range.
Prior to exposure to methanol, fibroin was considered to be in the amorphous Silk I phase that represents a water-soluble form naturally existing in the silk gland. As reported, exposure to alcohols can induce the transformation from Silk I to Silk II phase which, however, involves an irreversible crystallization process of self-assembled β-pleated-sheets. The fact that the response reported here is reversible indicates that methanol vapors induce only a small number of crystallized sheets located on the surface of the silk fibroin film. Because the sensor is operating in the absence of water molecules, that typically induce swelling and dissolution effects on an amorphous fibroin, the material cannot fully refold its structure in β-sheet crystallites and hence the total transition from Silk I to the Silk II becomes inhibited. For this reason, the fibroin overlayer corresponds predominantly to the Silk I phase.

Ongoing studies are focused on examining the response of the sensor to other VOC vapors and the effect of humidity. Exposure to saturated isopropanol vapors induced no change in either the wavelength or the strength of the attenuation band thus it can be concluded that the sensor is insensitive to isopropanol. For ethanol vapors, preliminary experiments indicated that sensitivity exists. Additional studies are currently underway to quantify the response of the sensor to ethanol and examine if selectivity, based on a dissimilar response for different alcohols, can be achieved.

4. CONCLUSIONS

We have demonstrated the first application—to the best of our knowledge—of silk fibroin as an active transducer on an optical fiber for the development of a methanol sensor. Employing an optical fiber long period grating and a silk fibroin overlayer sensing response in the presence of methanol vapors was confirmed with a sensitivity of 0.22 nm/mbar for the range 80 to 100 mbar.

ACKNOWLEDGMENTS

M.K. and S.P acknowledge financial support by the European Union’s Horizon 2020 research and innovation programs LASERLAB-EUROPE (871124), ACTPHAST 4.0 (779472) and the GSRT HELLAS-CH (MIS 5002735).

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