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Poly(vinyl alcohol) hydrogel based fiber interferometer sensor for heavy metal cations

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ABSTRACT

A Mach Zehnder fiber interferometer is demonstrated for sensing of the heavy metal cation, Ni^{2+} using a responsive poly(vinyl alcohol) (PVA) based hydrogel. The presence of Ni^{2+} increases degree of cross linkages within the hydrogel and increases its refractive index, leading to phase shift in the interferogram. Ni^{2+} concentration is monitored by the shifting of interference dips with a sensitivity of 0.214 nm/μM and limit of detection of 1 nM. Design of the PVA hydrogel to optimize sensitivity is discussed and the capability of the gel to immobilize various receptors enables a flexible platform for sensing applications.

1. Introduction

The use of heavy metals in modern industries has led to an ever increasing environmental burden. These metals (e.g. Hg, Pb, Ni, Cu, Cd, Zn, As) are non biodegradable and accumulate in the ecological systems, posing a serious threat to human due to its toxicological and carcinogenic effects. High exposure to Ni, for instance, can lead to cardiovascular, lung and kidney diseases and even cancer through altering of cellular metabolism, gene expression, gene repair and increased oxidative stress [1].

Such is the adverse effect on human health that there is active research in new sensing strategies for trace heavy metals [2] and various health and environmental agencies have set standards on maximum allowable heavy metals.

Current techniques for trace heavy metal detection require costly and sophisticated equipment like atomic absorption spectroscopy and inductively coupled plasma atomic emission spectroscopy that are operated by highly trained personnel, driving the need for inexpensive alternatives that could be rapidly adapted for continuous, remote monitoring applications.

Miniature fiber optic sensors capable of remote sensing offer a plausible alternative for trace metal sensing in the environment. Over the years, various fiber optics including fiber Bragg grating, long period grating and various fluorescence/absorbance, surface plasmon resonance based systems have been proposed for a vast array of sensing applications [3]. Recently, fiber-based interferometry has emerged and its sensing capability is widely explored owning to its inherent sensitivity, accuracy and dynamic range [4].

The basis of interferometry lies in the splitting and recombining of an initial coherent light. As a result of light splitting, part of the original light interacts with the measurand and incurs a phase difference with respect to the rest of the light. As a result, when the light is recombined, an interference pattern is observed. A phase shifting of the interference pattern is obtained when the measurand is changed and is the principle underlying interferometry-based sensors.

Various fiber interferometers have been demonstrated and reviewed in Ref. [4]. The most common interferometers include the Fabry Perot, Sagnac, Mach Zehnder and Michelson configurations.

The Fabry Perot fiber interferometer (FPI) relies on the interference of reflected beams off two surfaces that enclose an optical echelon. Tierney et al. [5] fabricated a FPI glucose sensor by coating responsive gel on the distal end of a single mode fiber. The gel serves as an optical echelon and volume transitions in presence of glucose alters the optical path length of the echelon that is used to infer glucose concentration. Chen et al. [6] proposed an FPI immunosensor

Abbreviations: ATR-FTIR, attenuated total reflection-Fourier transform infrared spectroscopy; EDCN, (3-dimethylaminopropyl)-N′-ethylcarbodiimide; FESEM, field emission scanning electron microscopy; LOD, limit of detection; 8HQ, 8-hydroxyquinoline; NHSN, hydroxysuccinimide; PAA, poly(acrylic acid); PCF, photonic crystal fiber; PVA, poly(vinyl alcohol); UV, visultra violet-to-visible wavelength range spectroscopy.

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by utilizing a suspended membrane that encloses one end of a hollow fiber. Immobilized Ig-G on the membrane binds specifically to anti-IgG, thus increasing the membrane's optical thickness. However, the Fabry Perot configuration suffers from an indirect readout. Post processing of the interference spectrum like frequency transforms and model fitting is necessary to demodulate optical path length changes. In addition, by using responsive gel as the optical echelon, a thick gel coating on the order of tens of micrometer (approximately 60 μm in Tierney's work [5]), is required in order to observe interference fringes within a reasonable bandwidth and this may limit the responsiveness of the sensor since volume transition of the responsive gel is often a diffusion limited process.

The Sagnac interferometer is based on the interference between orthogonal modes guided in a high-birefringence fiber. There are few reports of the Sagnac interferometer for chemical sensing. Chen et al. [7] coated a polarizing maintaining fiber (PMF) with moisture sensitive Chitosan and enclosed this fiber within a Sagnac loop to realize a relative humidity sensor. Swelling of Chitosan in presence of moisture exerts a uniaxial stress on the PMF that disrupts the geometry of the fiber core, altering its birefringence properties. Wang et al. [8] reported a relative humidity sensor based on similar principles using poly(vinyl alcohol) coated PMF. Both sensors require significantly longer sensing segment (50 cm and 6 cm respectively) and hazardous chemical etching of fiber is required to attain comparable sensitivity (81 pm/RH and 111.5 pm/RH respectively) to a Mach Zehnder based sensor (99.5 pm/RH using 3.8 cm sensing fiber) [9].

The operation of the Michelson interferometer is similar to the Mach Zehnder in involving the splitting and recombination of light except it works in the reflection mode. Although it offers the potential for a more compact sensing probe, it involves a more elaborate fabrication process and extra components like an optical circulator or coupler to guide the reflected light to the photodetector.

Hence, the Mach Zehnder interferometer (MZI) offers significant advantages over other interferometer configurations in its facile setup, direct readout and high sensitivity. Here, we realise an all fiber Mach Zehnder interferometer by splicing a photonic crystal fiber (PCF) between normal single mode fiber (SMF) similar to Ref. [10]. A thin submicron layer of poly(vinyl alcohol) (PVA)/poly(acrylic acid) (PAA) hydrogel film is coated onto the fiber via dip coating method and chemically modified to be sensitive to Ni^{2+}. The hydrogel film is characterized using field emission scanning electron microscope (FESEM) and attenuated total reflection-Fourier transform infra-red (ATR-FTIR) and various design considerations are studied to optimise sensitivity of the hydrogel interferometry sensor. The facile method of coating thin PVA/PAA hydrogel films and the ease in which the film can be modified with various receptors enables the setup to be adapted for other sensing applications.

2. Sensor descriptions

2.1. Fabrication of the fiber MZI

Optical fibers including SMF (8.2/125 μm SMF-28) and PCF (10.1/125 μm LMA-10) are purchased from Corning and NKT Photonics respectively. LMA-10 is a silica PCF that confines light within a 10.1 μm solid core that is surrounded by a regular hexagonal array of air holes and is used for the sensing portion of the MZI.

A 30 mm segment of PCF is spliced in between SMF using an electric arc splicer (Type 39, Sumitomo). All fibers are stripped of the acrylate jacket and the ends are cleaved using a precision fiber cleaver (Fujikura, CT-30) prior to splicing. The fibers' ends are aligned manually and an electric arc of optimized power and duration is applied to fuse the fibers. A length of air holes at the splice joint is collapsed in the process due to interfacial tension when silica is melted. The fiber interferometer is mechanically sound and able to withstand the splicer's inbuilt tensile test.

2.2. Coating PVA/PAA hydrogel on fiber MZI

PVA (Mw 89,000–98,000, Sigma–Aldrich) and PAA (Mw 100,000, Sigma–Aldrich) are added to deionized water (resistivity 18.2 MΩ cm, Milli-Q) in the required amount to make 10 wt% polymer blend. This is stirred in 80 °C water bath for 2 h to ensure complete dissolution and left to cool overnight with continuous stirring.

The PCF segment of the MZI is immersed in piranha solution (sulphuric acid and hydrogen peroxide in 7:3 volume ratio) at 80 °C for 60 min and rinsed thoroughly with deionized water before drying under stream of purified nitrogen gas. The piranha treatment removes any organic residue and hydroxylates the fiber surface.

A dip coater (KSV NIMA) is used to dip the optical fiber into the polymer blend and withdrawn at a constant speed of 100 mm/min. A thin film of polymer blend coats the fiber and is dried under room temperature conditions before heating in a 130 °C furnace (Carbolite). The fibers are then left to cool before immersing in deionized water to remove excess polymers that have not been cross linked.

2.3. Chemical modification of PVA/PAA hydrogel

The PVA/PAA hydrogel coated fiber is immersed in pH 6 phosphate buffer (Sigma–Aldrich) consisting 0.13 M N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide (EDC, Sigma–Aldrich) and 0.33 M N-hydroxysuccinimide (NHS, Sigma–Aldrich) for 60 min followed by immersion in 0.01 M 5-amino-8-hydroxyquinoline dihydrochloride (Sigma–Aldrich) prepared in 0.1 M tris(hydroxymethyl)aminomethane) (Sigma–Aldrich) pH 7.3 buffer for 4 h.

The fiber is kept in deionized water to remove any unreacted materials until use.

2.4. Experimental setup

Broadband light source (AS3223-BA2) with emission wavelength from 1530 nm to 1605 nm is used to interrogate the fiber interferometer at one end and the transmitted light is recorded by an optical spectrum analyzer (AQ6370, Yokogawa) at the other (see Fig. 1). The PCF segment is fixed between 2 fiber holders in a custom made chamber that allows the immersion of the PCF segment in various sample solutions. All spectra are later processed using MATLAB (MathWorks) and plotted using OriginPro 8 (OriginLab).

3. Principles of operation of the fiber MZI

The LMA-10 PCF is designed to be endlessly single mode for all optical wavelengths. Its fundamental mode that resembles a quasi Gaussian beam is confined within the core and is also termed the core mode.

The LMA-10 is spliced in between SMF and forms the sensing segment of a MZI. The air holes at the splice intersection are deliberately collapsed at the splice intersection to from a uniform silica region (approximately 270 μm in length) where light confinement is lost (see Fig. 2a). Light propagating from the SMF to LMA-10 diffracts as it transverses the collapsed region [11]. The enlarged beam thus excites core and higher ordered modes within the LMA-10. These higher ordered modes are usually not propagated by the fiber and suffer high optical losses. The transverse profiles of these higher orders modes show significant optical energy residing within the cladding of the optical fibers and are thus also known as cladding modes.