



Detection of low-concentration heavy metal ions using optical microfiber sensor



Wen Bin Ji^{a,*}, Stephanie Hui Kit Yap^{a,1}, Nishtha Panwar^a, Li Ling Zhang^a, Bo Lin^b, Ken Tye Yong^{a,*}, Swee Chuan Tjin^{a,*}, Wun Jern Ng^c, Maszenan Bin Abdul Majid^c

^a Centre for OPTIMUS, School of Electrical and Electronic Engineering, Nanyang Technological University, 639798, Singapore

^b China Academy of Electronics and Information Technology, Beijing, 100041 China

^c Nanyang Environment and Water Research Institute, Nanyang Technological University, 637141, Singapore

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ABSTRACT

Heavy metal pollution in natural water environment is always a concern in both human and ecosystem health. All current systems available in the market for detecting heavy metal ions have common drawbacks such as bulky size, expensive set-up and costly maintenance. This paper presents an optical microfiber sensor functionalized with chelating agent to detect the existence of specific heavy metal ions of low concentration. To the best of our knowledge, coating of chelating agent on silica microfiber of very small diameter (3.9 μm) is the first such report. A clear spectral shift was observed when the sensor was immersed into metal ion solution of concentration 10 ppb.

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1. Introduction

Most heavy metals (for example, Pb, Cu, As, Zn, Cd) are lethal at high concentrations, nevertheless they can be deleterious even at very low concentrations, because they get accumulated in human organs, causing long term negative health effects [1]. Alarming high levels of heavy metal concentration have been found in drinking water sources in Asian countries like China, Bangladesh, Thailand, Nepal and India [2]. For instance, high arsenic compound (107 $\mu\text{g/l}$) found in drinking water consumed by India's population is approximately 11 times higher than the maximum permissible limit set by World Health Organization (WHO) [3]. Besides building an efficient heavy metal water filtration system, continuous monitoring of heavy metal contamination in natural water environment is equally important to ensure safe drinking water for the sake of human health.

Conventional ways of quantitatively detecting levels of heavy metal contamination include atomic absorption/emission spec-

troscopy, inductively-coupled plasma mass spectrometry and cold vapor atomic fluorescence spectrometry [4]. Albeit these methods provide good measurement sensitivity, they involve complicated chemical processes for extracting metal ions from sampled water collected from reservoir of interest. Moreover, sophisticated instrumentation involved in these techniques does not encourage real time, on-site detection to be carried out and the cost of these instruments are usually very high.

As a result, there is growing demand of a rapid on-site heavy metal detection system that is low cost and does not involve complicated operation procedures. One feasible solution for this matter is to use optical fiber sensors, taking advantage of their fascinating characteristics- compact in size and light in weight, suitability of use in harsh environment, remote sensing capability, and ease of implementation in any structure due to their small size [5]. Various configurations of optical fiber structures, each with unique design and optical properties have been explored to fit the needs of a particular sensing system. These systems such as the microfiber coil resonator based sensor [6], the double-pass in-line fiber taper Mach-Zehnder Interferometer (MZI) sensor [7], and the microfiber mode interferometers [8–11], have all demonstrated good sensing capabilities. Among all reported fiber structures, the tapered microfiber occupies a prominent place due to its outstanding achievable sensitivity and low fabrication cost.

* Corresponding authors.

E-mail addresses: jiwe0003@e.ntu.edu.sg (W.B. Ji), ktyong@ntu.edu.sg (K.T. Yong), esctjin@ntu.edu.sg (S.C. Tjin).

¹ These authors contributed equally to this work.

The key feature of heavy metal detection chemical sensors is a unique chemical compound known as chelating agent, which binds to a specific metal ion, and is used to identify and quantify its concentration. Chelating agents are organic compounds (i.e. compounds whose molecules contain carbon), often used in metal intoxication medical treatment due to their ability to form a stable metal chelates (i.e. compound composed of metal ion and chelating agent) that are easily excreted from target site. These compounds should be wisely chosen for detection of the target analyte of interest. Moreover, upon successful detection of analyte, they should be able to transform into a measurable physical change for analytical purposes. These chelating agents are adhered onto the sensing surface, and the technique adopted in attaching them to the surface plays a critical role in sensor development and optimization. Many developed fiber optic chemical sensors found in literature often involve chemical modification of the optical fiber surface [12,13]. This is because the common optical fiber is made of inorganic material (silica) and it requires functionalization of the fiber surface prior to attachment of organic substrate/compound on it. Once the fiber surface is ready to bind with organic substrate/compound, a crosslinker, which acts as a bridge, is needed to create a strong bond between them. The substrate/compound layer developed on the fiber surface then reacts with the target analyte, causing variation in the intensity of the light travelling down the fiber. Since the intensity change is related to the analyte concentration, quantitative analysis can be performed to detect the precise levels of analyte.

In our work, chelating agents for detecting specific heavy metal ions were coated on microfiber surface having a diameter of less than 4 μm . Although several researchers have demonstrated surface-modified tapered microfiber as heavy metal sensor with low detection limits [13,14], chemical functionalization on such small diameter silica microfiber is still a new area to explore to the best of our knowledge. Besides the challenge of achieving a uniform and stable coating on a small diameter microfiber, the cross sensitivity of such microfiber is another issue that needs to be addressed properly. The strong evanescent field exposed to the surrounding makes it sensitive not only to refractive index but also to strain and temperature [15–17]. We have successfully modified the current protocols of coating chelating agents in each coating stage and designed a sensing system to eliminate the cross sensitivity effect, and obtained promising and reliable results.

2. Experiment

2.1. Fabrication of microfiber

The conventional way of fabricating a microfiber is the flame brushing method wherein a fusion splicer or a CO_2 laser is used to soften the optical fiber coupled to a mechanical setup for stretching the fiber. These microfibers normally have diameters of a few micrometers. In our work, a fiber drawing machine (Vytran, GPX-3000) with motorized fiber holding stages is utilized. To be used as a refractive index sensor, the microfiber is usually tapered as thin as possible in order to achieve high sensitivity. However, limitation in the measuring range of refractive index is observed for most of these interferometer-based sensors. As the wavelength responses of these modal interferometers appear in a periodic fashion, it is impossible to identify how much the resonant wavelength has shifted once the wavelength shift due to the change of external medium exceeds the free spectral range (FSR). It is known from previous studies that the most dominant parameters to form a desired fiber taper are the heating power and the pulling speed, thus the trade-off between the sensitivity and the measuring range has been well addressed by tapering an ultra-short waist microfiber [18].

The tension monitor of the microfiber fabrication machine is used to calibrate the normalized power of the graphite filament as well as its respective power degradation rate for microfiber fabrication. The power is close to the normalized value when the fiber tension detected by the monitor during the fabrication process is maintained at a certain positive level with slight periodic fluctuations. In this work, the normalized power of the filament was calibrated to 50 W and the power degradation rate was -15% during the waist drawing period. The fabricated microfiber has a diameter of 3.9 μm and its total length is around 8 mm with left transition 2.4 ± 0.5 mm, waist length 4 ± 0.5 mm and right transition length 1.6 ± 0.5 mm. The resulting FSR is 20 nm, which is safe for detection of slight perturbation on the microfiber surface [18].

2.2. Microfiber surface modification

Surface treatment of fabricated microfiber is accomplished by soaking the microfiber into engineered chemical solvents. The treatment process begins by washing the microfiber in acetone solution for ten minutes in order to remove dust particles, contaminants or other impurities on the fiber surface. Prior to silanization, the microfiber was cleaned with 1 M sulphuric acid (H_2SO_4) for 30 mins at 90°C , followed by Piranha solution (mixture of sulphuric acid and hydrogen peroxide in a volume ratio of 3:1) for 10 mins inside fumehood and 1 M sodium hydroxide (NaOH) for 10 mins at 120°C . Between each of these cleaning steps, the microfiber was rinsed thoroughly for a few times with deionized (DI) water. This step is important to generate high density of hydroxyl functionalities necessary for silane modification. Next, two percent of silane coupling agent, 3-Aminopropyltriethoxysilane (APTES), was mixed into DI water at pH 4.5–5.5 (adjusted by acetic acid). The microfiber was dipped into the solution for two hours at 75°C under low humidity environment. Silanized microfiber was then dried overnight in an oven at 60°C . Following this, each 1 ml of carboxyl groups containing chelating agent solution such as Ethylenediaminetetraacetic acid (EDTA) were activated using 0.4 mg of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and stabilized by 1.1 mg of *N*-hydroxysuccinimide (NHS) and left undisturbed for 15 min at room temperature. The activated chelating agent was then added to the silanized microfiber and left undisturbed for 2 h to allow covalent bonds to be formed. In the end of the bonding reaction, 10 mM hydroxylamine was added to stop the reaction. A schematic illustration of the surface functionalization protocol is shown in Fig. 1.

2.3. Scanning electron microscope (SEM) imaging

Fig. 2(a)–(b) illustrate the surface of fiber samples at different stages of functionalization process. In order to see the surface clearly, the fiber used in these three figures is 125 μm . Under large magnification, uniform layer of APTES was seen on silanized sample, which indicates even coating and sufficient sites for the attachment of chelating agent. On the other hand, apparent increase in surface roughness was seen in Fig. 2(c) on a fiber sample that has been tested with lead(II) ion solution. This roughness can be attributed to the various stages of chemical functionalization on the microfiber surface. Furthermore, Fig. 2(d)–(f) illustrate the microfibers' entire surface images in different coating stages. It can be seen that the results are consistent with the first three pictures that surface roughness increase as the coating progressed. In each figure, different microfibers were used for imaging as the microfiber is impaired once it is stucked onto round pallet in the chamber and there is no way to reuse it for next coating stage. It is also due to this, thickness of the film is currently not possible to view as we need to view under SEM before we functionalize them. However, after taking out the microfiber from the SEM, the

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