Corrugated Fiber Grating for Detection of Lead Ions in Water

Yasser Chiniforooshan, Jianjun Ma, Wojtek J. Bock, *Fellow, IEEE*, Wenhui Hao, and Zhi Yuan Wang

***Abstract*—Optical fiber fluorescence sensors are widely used for chemical sensing. Intrinsic fluorescence sensors such as evanescent-wave sensors can be used for surface sensing while extrinsic sensors are used for bulk sensing. In intrinsic/extrinsic fluorescence sensors, typically the side-wall/end-face of a single/multimode fiber is used. In this paper, we introduce a novel intrinsic optical fiber fluorescence sensor which uses the side-wall of a large-core multimode fiber to collect the fluorescence from the bulk of samples. The method is to use a corrugated fiber grating, fabricated by a CO_2 laser, to couple radiating modes to the core modes. Using the sidewall of a fiber helps to fabricate a multitarget or a distributed sensor. We also report the sensing of Lead ions with concentration as low as few ppb in water using a fluorescence turn-on polymer as a chemical probe.**

***Index Terms*—CO_2 laser, corrugated fiber grating, fluorescence, lead detection, optical fiber sensor, trace element concentration.**

I. Introduction

In recent years optical methods became one of the most reliable and precise sensing methods for selectively tracing the chemical or biological compounds. While there are lots of interests on direct optical sensors for higher sensitivity [1], the indirect optical sensors are widely studied and used for chemical and biological sensing. Although fluorescence sensors, as indirect such optical sensors, are developed and globally used since decades ago, they are still the most popular sensors in this field because of their high selectivity, simplicity and sensitivity [2].

On the other hand, optical fiber as a medium for light propagation is a simple and reliable platform which can be used either to carry the sensing signal or to transduce the chemical event into the optical signal and carry it to detection system. Based on the role of optical fibers in sensing process, the optical fiber sensors are called extrinsic or intrinsic. In an extrinsic fiber optic sensor the fiber just carry the sensing signal, while in an intrinsic one the fiber transduces the external chemical event into an optical signal as well.

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The application of optical fiber for fluorescence sensing, or so-called optical fiber fluorescence sensor (OFFS), in life sciences and in chemical sensing is addressed in many papers. For instance, a traditional intrinsic OFFS is evanescent-wave fluorescence sensor which was studied first by Fahrenfort [3]. A typical evanescent-wave sensor is used to detect the external events on the surface of optical fiber side-wall. Typically, a single-mode fiber suits for this purpose well because the evanescent tail of electromagnetic wave penetrates more into the fiber surroundings comparing to the multi-mode fibers [4]. Therefore the surface sensitivity of this type of fluorescence sensor is high, while it is not recommended for detection of the targets far from the fiber side-wall because of its poor bulk sensitivity.

There are various architectures for extrinsic OFFSs which transfer the fluorescence signal from the sensing medium to the detection system including multi-mode fiber [5], microstructure fiber [6], or a bundle of fibers [7]. All those use end-face of optical fiber that could be beveled, spherical or flat for different applications [8]. For each application in different mediums, the structure should be designed such as the fluorescence collectivity would be maximized while the excitation trace on the detector would be minimized. Bifurcated and/or beveled end-face is a common structure for this purpose. One of similarities of most extrinsic OFFSs is that they use the end-face of the multi-mode fiber for fluorescence collection. The reason is that the numerical aperture of the multi-mode fiber at its end-face is bigger than in single-mode fiber.

These two main types of OFFSs, intrinsic evanescent-wave and extrinsic OFFS, have their own limits. Regarding to the receptor material on the side-wall of the fiber, evanescent-wave sensor is very sensitive to specific events occurring within the immediate layer around the fiber with thickness in the order of wavelength. However, the fluorescence intensity (FI) is very weak due to the fact that there would be few fluorophores in this thin layer as well as due to the low evanescent-core mode coupling efficiency which is as low as 2% to 8% of total intensity [9]. Therefore, a long length of sensing area is needed in addition to tapering of the fiber [10]. Thus using this as a multiplexed or distributed sensor is challenging. On the other hand, in extrinsic OFFSs the collection efficiency of the fluorescence signal is much higher because it collects fluorescence from all the layer of the bulk medium and the coupling from the end-face is more efficient than from the side-wall. However in this case, because of the end-face usage, the sensor cannot be used as a multiplexed or distributed sensor. It also cannot determine the depth where an event has occurred.

Contamination of the water and soil with heavy metals is increasing as a result of industrial, municipal and agricultural

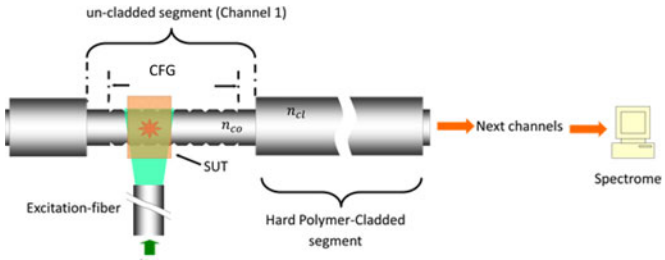


Fig. 1. Optical fiber fluorescence sensor enhanced by corrugated fiber grating.

activities. Lead ion as a heavy metal is highly toxic and can be absorbed by plants and animals and entered into the human body. On the chemical side, the chemical probes should be used for selective sensing. There is a variety of mechanisms that are used for chemical probing. Among them, fluorescence turn-on [11] and quenching [12] are well-known, simple and widely used processes. Although conjugated polymers have been explored for amplified fluorescence detection, there are few reports on fluorescence turn-on polymer sensors for selective detection of Pb^{2+}.

Therefore, it would be more beneficial if an optical fiber sensor can use short length of fiber side-wall with higher collection efficiency than evanescent sensors, and can have an ability to scan different layers of a medium that usually contains low quantum yield fluorophores. In addition, the use of the fluorescence turn-on polymer probe for detection of Lead ion in water can increase even more the sensitivity and selectivity of the sensing device. These are the goals of introducing novel type of intrinsic optical fiber fluorescence turn-on sensor in this paper with more details than it was briefly presented in OFS-23 conference [13] for detection of Pb^{2+} in water.

II. Sensor Structure

The OFFS which is proposed in this paper constitutes of a highly multi-mode optical fiber with corrugated fiber grating (CFG) fabricated along the fiber on its un-cladded side-wall. The common application of the long period fiber gratings imprinted on single-mode fibers is to couple the core mode to the cladding modes at a certain wavelength. This causes a resonance in transmission spectrum for that specific wavelength [14]. Unlike that common role in case of the single-mode fibers, we use a CFG imprinted on highly multi-mode fiber to couple the cladding modes to the core modes within a certain range of wavelengths. Cladding modes are excited by the fluorophores covering the fiber side-wall. Because of the wideband nature of the fluorescence spectrum, the coupling over the range of wavelengths would be beneficial for fluorescence detection applications.

This fluorescence is originated from a chemical probe covering fiber side-wall. The chemical probe will selectively catch the chemical target and fluorescence will be released by their molecular reaction.

The proposed multi-segment OFFS is shown in Fig. 1. The sensor consists of two segments, a un-cladded and a hard polymer-cladded segment. There is the CFG fabricated on the un-cladded segment as well as the sample under the test (SUT) which is placed on it. The SUT is simply a few drops of a liquid sample that may contain the chemical target ions. It has been already mixed with chemical probe. The chemical probe as mentioned previously is a sensitive fluorescence turn-on polymer which is selective to the target ions [15]. The target ions in this case are the Lead ions, and the fluorescence will be turned-on in the presence of Pb^{2+}.

If SUT is contaminated by the Lead ions, the fluorescence would be released in SUT. The refractive index of SUT is close to the water refractive index (1.33) which is lower than the core refractive index (1.46). The core modes of a fiber have effective indices n_{eff} between core n_{co} and cladding n_{polymer} refractive indices: $n_{\text{polymer}} < n_{\text{eff}} < n_{\text{co}}$. On the other hand, all fluorescent light propagating in SUT has effective index less than the water refractive index. Therefore the fluorescent light cannot excite the core modes of the fiber and they would exist as radiating modes. Excluding the small portion of evanescent coupling, this fluorescent intensity has huge loss and would radiate out of the fiber within a short distance unless radiating fluorescent intensity is coupled to the core modes. The role of the CFG in this sensor is to perform this coupling between the radiating and the core modes. By optimizing the parameters of the CFG for a certain fluorescent wavelength we could efficiently couple the fluorescence to the core of the fiber and let the fluorescent light propagate inside the core toward the detection system. It can be shown that the fluorescence released in a certain radial distance from the side-wall can be optimally coupled to the core of the fiber. This distance also can be set by controlling the CFG parameters. By doing so, we can focus on the events happening in certain layer around the fiber [16]. Another parameter that needs to be considered is the length of the SUT along the fiber. Since a very short SUT leads to the low fluorescent intensity and a very long SUT causes the high loss for the released fluorescence, therefore there is an optimized length in which the fluorescence collection efficiency could be maximized.

III. Fabrication

The CFG is fabricated using a CO_2 laser beam and is optimized by the choice of grating parameters (periods, length, depth, etc.) for certain fluorescence wavelength. The grating can be fabricated on the fiber side-wall by exposing it to a low energy IR radiation that would slightly change the refractive index in both core and cladding. Another way is to project the higher radiation energy to corrugate the fiber side-wall. Typically the corrugated gratings are strong gratings, with few periods resulting in coupling between the modes being strong. Fabrication of those periods can be done by moving a laser beam along the fiber or moving the fiber under a fixed laser beam and applying some weight to the fiber. Fig. 2 shows the setup to fabricate a CFG on a multi-mode fiber.

To set all the parameters for more efficient fluorescence collection, a standard fluorescent solution is used. This solution is a Rhodamine 6G with concentration of $10.3\,\mu\text{g/ml}$ in water. By changing the period it is concluded that there is a specific period

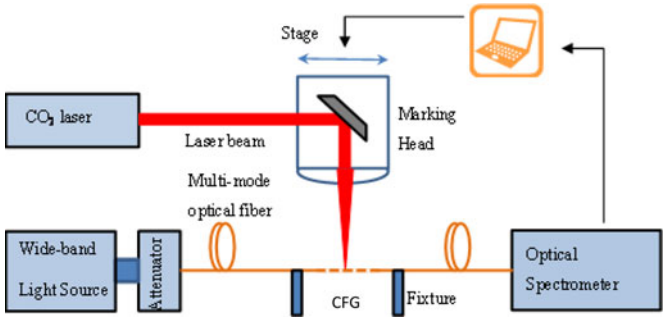


Fig. 2. Corrugated fiber grating fabrication setup using a high power CO_2 laser.

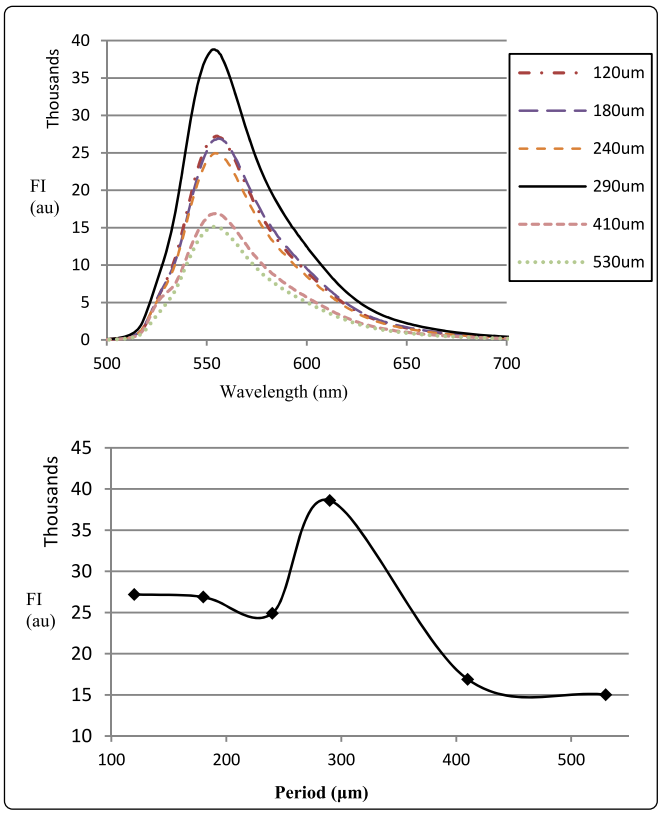


Fig. 3. Fluorescence signals for different periods of CFG and the calibration curve at maximum intensity.

in which the coupling of radiation modes to the core modes in certain wavelength range would be maximum. Fig. 3 shows the experimental data confirming that the optimized period is 290 μm.

The number of periods in a periodic structure defines the percentage of coupling between the two classes of modes. To achieve the highest collection efficiency there is an optimized number of periods that should be written on the fiber. By making the different number of periods and test them with the standard R6G fluorophore solution it is possible to find the optimized number. Fig. 4 shows the optimized number of periods for the fluorescence in the range of visible light.

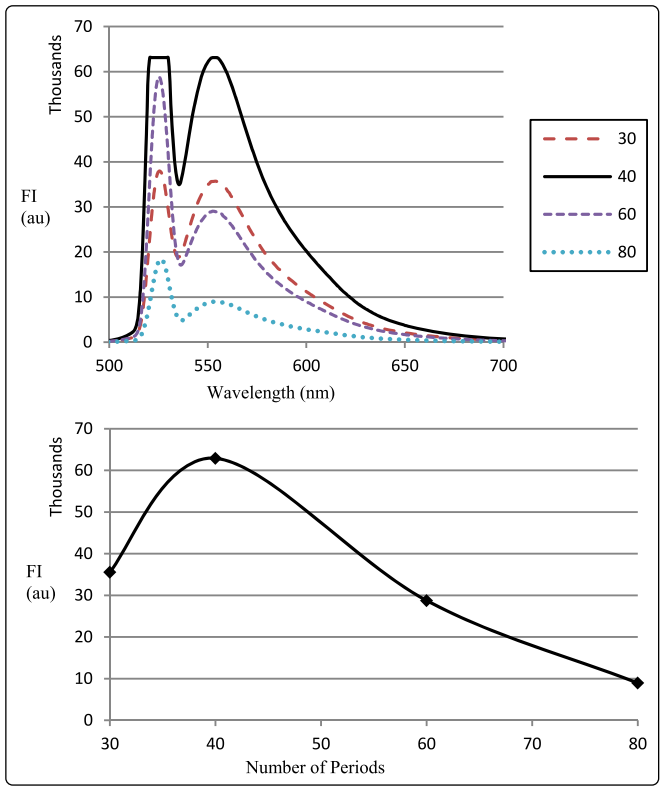


Fig. 4. FI collected by sensors with different number of periods and the calibration curve at maximum intensity.

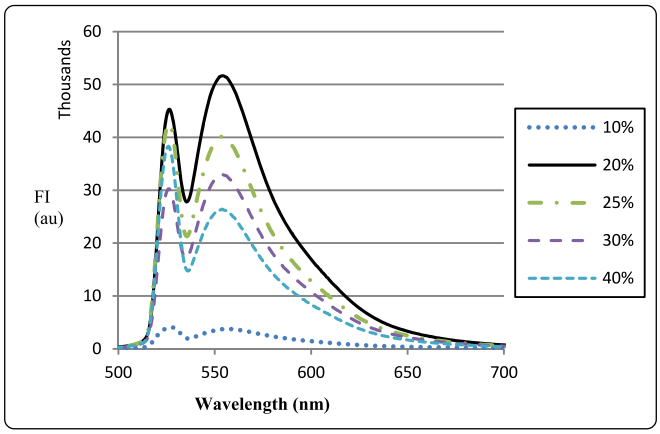
The depth of the grooves which are made by projecting the laser power to the fiber also affects the strength of the coupling. Since the excited fluorescence is produced around the fiber, therefore, the intensity is distributed mostly around the edge of the fiber. Very deep grooves may not be as good as shallower ones but very shallow grooves will also not be able to completely affect those higher-order modes. There is an optimized depth of grooves that can affect all the intensity of the higher order modes and at the same time, not to affect the coupled modes of lower orders. Fig. 5 shows the optimum laser power for making the efficient grooves.

Consequently, the optimized CFG has the 40 periods with the seperation distance of 290 μm. The laser power has to be set to about $2w$ for the best result.

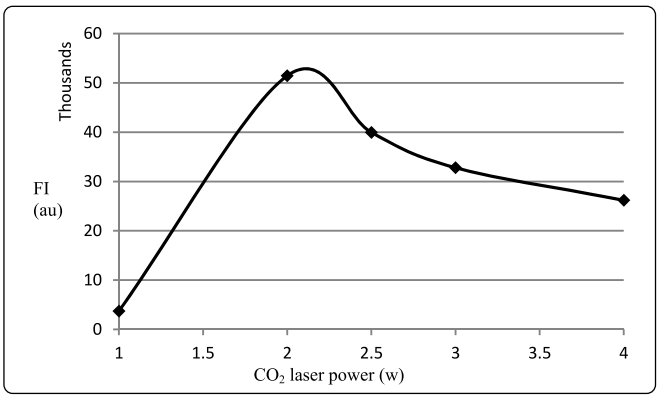
IV. Measurements

The measurement setup is shown in Fig. 6. The SUT can be sucked up from the sample container by a pipet which has been drilled to pass a large-core multi-mode fiber through it. The sample is excited by a collimated LED light at the excitation wavelength and perpendicular to the fiber axis. To test the sensitivity and limit of detection for this sensor some water solutions with different concentration of the Lead ions has been prepared.

In Fig. 7 the experimental peak value of the fluorescence captured by the sensor for different Lead concentration in water is shown. There are two errors in this measurement. First is the



(a)



(b)

Fig. 5. (a) Fluorescence signals for different power of CO_2 laser that leads to different depths of grooves on the fiber side-wall. (b) Maximum FI collected by sensors with different depths of grooves related to the CO_2 laser power.

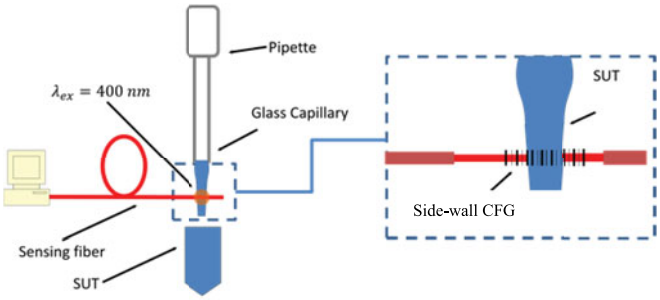


Fig. 6. Instrumentation set-up of the optical fiber fluorescent sensor exploiting fluorescence collection from the side-wall of a multi-mode fiber.

error on determination of the measured lead concentration. This error is calculated to be 0.1 μg/L or 0.1 ppb.

Second source of error is the FI measurement error on set-up shown in Fig. 6. The FI measurement error is 7% of the total fluorescence change. Consequently, Fig. 7 shows that the minimum concentration of the lead ions that can be detected by this sensor using the measurement setup shown in Fig. 6 is about 1 μg/L or 1 ppb.

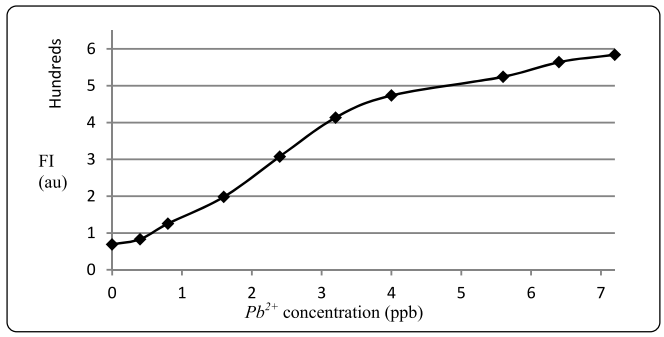


Fig. 7. Lead ion concentrations in water detected by fiber optic fluorescence sensor that is enhanced by corrugated fiber grating.

Since this sensor uses small length of the side-wall (less than 2 cm) there is a possibility of using also another channel along the fiber to detect in parallel different chemical material with its specific chemical probe.

V. Conclusion

In Conclusion, we developed an intrinsic optical fiber fluorescence sensor for detection of Pb^{2+} in water. The chemical probe that was used for this sensor is a novel fluorescence turn-on polymer which is selective to Lead ions. An optimized corrugated fiber grating imprinted on the side-wall of a large-core multi-mode fiber was used to collect fluorescence from not only the surface but also from the bulk of the sample. Therefore, the sensor can be used as a multi-target or as a distributed sensor. The Environmental Protection Agency (EPA) has strictly regulated the concentration of Lead ion in drinking water not to exceed 15 μg/L (or 15 ppb) [17]. The experimental results show that the detection limit of the Lead ions concentration for this sensor is much lower than the limit for Lead contamination of drinking water as introduced by EPA regulation.

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