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2015

Ravikumar, R., Chen, L. H., Chan, C. C., So, P. L., Tou, Z. Q., & Peng, Z. (2015).
Chitosan-hydrogel-based fiber optic sensor for heavy metal ion detection. Proceedings of
SPIE - 24th International Conference on Optical Fibre Sensors, 9634, 963440-.
doi:10.1117/12.2194804

<https://hdl.handle.net/10356/88345>

<https://doi.org/10.1117/12.2194804>

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Chitosan hydrogel based Fiber-Optic Sensor for Heavy metal ion detection

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ABSTRACT

A no-core fiber (NCF) based intermodal sensor for nickel ion (Ni^{2+}) detection is proposed. Bilayers of chitosan and Poly Acrylic acid (PAA) functionalized on the sensor surface serve as adsorption sites for nickel ions thereby causing change in refractive index (RI) along the cladding bilayer boundary. Nickel adsorption at different concentrations was monitored continuously through measurement of wavelength shifts. As observed, the proposed sensor exhibits Ni^{2+} detection sensitivity of 0.0237 nm/ μM .

Keywords: intermodal, no core fiber, fiber-optic interferometer, nickel ion sensor, chitosan

1. INTRODUCTION

Heavy metals contamination is a major threat because of toxicity and carcinogenic effects. This necessitates monitoring of these harmful species in water bodies. Recently, various sensing methodologies are being developed, however, they are usually associated with high cost, complex, time consuming and bulky etc.

In this paper, a miniature, fast response and low cost intermodal interferometer for Ni^{2+} sensing is proposed. A no core fiber (NCF) was spliced in between single mode fibers (SMF) to form an intermodal interferometer and the NCF surface was functionalized with a bilayer of chitosan and PAA to facilitate Ni^{2+} sensing. Nickel concentration variation induced spectrum shifts were monitored in real-time and the sensitivity of the sensor towards Ni^{2+} concentrations was preliminarily evaluated.

2. SENSOR FABRICATION

NCF is a pure silica fiber with an undoped core which has been used previously for refractive index sensing^[1]. Sensor fabrication involved splicing a piece of NCF (40 mm) with SMFs to form an intermodal interferometer and the chitosan/PAA functionalization on the NCF surface was carried out through electrostatic self-assembly (ESA) process, as chitosan is cationic in acids and PAA is anionic due to the present of functional groups such as amine and carboxyl groups. The chitosan/PAA bilayer offers a large number of Ni^{2+} adsorption sites to facilitate effective transduction of the sensor^[2].

To fabricate the sensor, the sensor was first treated with piranha solution for 30 minutes and washed with water and dried in a stream of nitrogen gas, which helps in making the surface anionic due to hydroxylation. The sensor was then dipped in 2% chitosan solution for 3 minutes, followed by rinsing in water for 60 seconds and dipped for 3 minutes in 4% PAA solution. Finally, the sensor was allowed to be dried overnight and entire process resulted in the formation of bilayer of chitosan and PAA on the sensor surface.

3. SENSOR CALIBRATION

NCF is a multiple mode waveguide and the higher modes can be excited by launching an input field through the lead in SMF. The interference of these modes leads to formation of self-images along the NCF [3]. The resultant spectral dip wavelength, λ_N can be expressed by Equation (1), where N_{NCF} is the effective refractive index at the core ambient interface, D_{NCF} the core diameter of NCF, and L the length of NCF segment. From the equation, λ_N is a function of N_{NCF} , D_{NCF} and L , since both D_{NCF} and L can be regarded as a constant, λ_N is only proportional to effective refractive index N_{NCF} .

$$\lambda_N = n \left(\frac{N_{NCF} D_{NCF}^2}{L} \right) \quad n=0,1,2,3,\dots \quad (1)$$

The schematic diagram of the sensing system is presented in (Fig. 1) which consists of a broadband light source (center wavelength: 1540 nm, full width of half maximum (FWHM): 70 nm), optical signal analyzer (OSA) (YOKOGAWA AQ6370) and the proposed sensor. To calibrate the sensor, the sensor without chitosan/PAA functionalization was tested by using different refractive index (RI) solutions and the spectrum was recorded by OSA (Fig. 2(a)). It is observed that with increasing RI, λ_N shifts to longer wavelength (red shift) which is in accordance with equation (1) as the N_{NCF} is modulated at the NCF ambience boundary. λ_N shift in response to different RI value is presented in Fig. 2(b), it is observed that the plot has two linear regions: 1.33 to 1.39 (low RI region) and 1.40 to 1.43 (high RI region). The sensitivity of the sensor is 144.64 nm/RIU and 550.9 nm/RIU respectively, which are relatively higher than other reported fiber optic RI sensors [4][5].

Figure 1. Schematic diagram of the NCF based interferometer

Fig. 2(a)

Fig. 2(b)

Figure 2(a). Spectral response of the bare NCF fiber in response to RI changes and

Figure 2(b). Calibration curve for measured wavelength shifts with external refractive index (Right)

4. RESULTS AND DISCUSSION

After calibration, the chitosan/PAA functionalized sensor was evaluated by using different Ni^{2+} concentration solutions. A stock solution of 10 mM concentration of NiCl_2 was prepared at pH 6 and various concentrations of Ni^{2+} were prepared by the serial dilution of the stock solution. The spectral response of the sensor was monitored and recorded (Fig. 3(a)). It is observed that with increase in concentration of Ni^{2+} ions, the interference pattern shifts to higher wavelengths, indicating an increment in RI at the cladding boundary due to the chelation/complexation of Ni^{2+} with the amino groups in chitosan [6]. As shown in Fig. 3(b), the Ni^{2+} sensitivity in the range of 300 μM was evaluated to be 0.0237 nm/ μM with R^2 value of 0.9997.

Fig. 3(a)

Fig. 3(b)

Figure 3(a). Spectral response of the functionalized sensor in response to various Ni^{2+} concentrations and

Figure 3(b). Linear fit curve for measured wavelength shifts with different Ni^{2+} concentrations

5. CONCLUSION

A heavy metal ion sensor using a fiber optic intermodal sensor has been demonstrated. Electrostatically self-assembly process was used for the functionalization of chitosan and PAA on the sensor surface to facilitate sorption of Ni^{2+} ions. The sensitivity of sensor to Ni^{2+} ions was determined to be 0.0237 nm/ μM . The sensitivity can be further improved by using a suitable ligand on the polymer matrix [7], which would be the focus of future work.

Acknowledgements

This work was supported by the ENERGY MARKET AUTHORITY (LA/CONTRACT NO. NRF2013EWT-EIRP001-006).

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