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Fiber optic Nickel ion sensor based on direct ligand immobilization

R.Raghunandhan^a, L.H.Chen^b, C.C.Chan^{a*}

^aDivision of Bioengineering, School of Chemical and Biomedical Engineering Nanyang Technological University, Singapore, 637457

*Email: eccchan@ntu.edu.sg

^bGLOBALFOUNDRIES, Singapore, 738406

ABSTRACT

An inline intermodal no core fiber (NCF) sensor based on direct ligand immobilization for detection of nickel ions (Ni^{2+}) is proposed. Covalently immobilized nickel specific ligand, Meso-Tetra(4-carboxyphenyl)porphine, on the NCF surface serves as adsorption site for Ni^{2+} and can induce ambient refractive index (RI) change around the NCF on occurrence of binding events. The change in RI results in spectrum wavelength shifts, which was measured for continuous monitoring of Ni^{2+} concentration. The proposed sensor was observed to exhibit a sensitivity of 121.03 nm/mM towards Ni^{2+} ions.

Keywords: no core fiber sensor, refractive index, nickel ion, ligand, direct immobilization

1. INTRODUCTION

Detection of metal ions in aqueous solution is carried out using conventional methods like anodic stripping voltammetry (ASV), inductively coupled plasma mass spectrometry (ICPMS) and atomic absorption spectroscopy (AAS). These methods are complex and involve tedious procedures for sample preparation, expensive, require extensive training to use and are destructive. This has led researchers to focus on optical sensors such as surface plasma resonance (SPR) sensors or optical fiber sensors as an alternative to the conventional methods. These sensors possess fast response times, don't require extensive sample preparation, and are non-destructive and cost-effective. In the last few years many fiber-optic based SPR sensors and fiber-optic interferometric sensors for ion detection have been demonstrated. The significant aspect of these sensors is the presence of an active chelating polymeric layer on the silica surface for specific detection of a target ion. The major problem encountered with polymeric based optical sensors is its lack of specificity to the target molecule, as the chelating groups in the polymer film can bind to other molecules/ions with a weaker force introducing false positive reading. In addition many polymers are ineffective at acidic pH values due to the protonation of functional groups such as amino or carboxylic acids. As a result, in low pH environment, they attain positive charge and are unable to donate electrons to the target molecules/ions to retain them in the polymeric network. Instability is attributed to the swelling effect of the hydrogel in the aqueous environment. Moreover, optical sensors generally operate based on the change of refractive index of the polymeric medium when target molecules/ions binding takes place. This swelling effect due to water adsorption or temperature will result in thickness/refraction index change of the polymeric film causing cross sensitivity error. To overcome these limitations an alternative sensing system for heavy metal ion detection has to be developed that doesn't require the use of a polymer matrix.

In this paper, a NCF based intermodal sensor for sensing of Ni^{2+} is demonstrated. The sensor was fabricated by splicing a length of NCF to a single mode fiber (SMF) and a Ni^{2+} specific ligand was covalently immobilized onto the sensor surface. The sensor spectrum shifts induced by change in Ni^{2+} concentrations were continuously monitored and the sensitivity of the sensor towards Ni^{2+} concentrations was evaluated.

2. SENSOR FABRICATION

NCF is a heterocore silica fiber with no cladding and an undoped core and has been previously reported for sensing applications^[1, 2]. The intermodal sensor is fabricated by splicing a 35mm length of nocore fiber (NCF) with a standard SMF fiber (Fig. 1 inset). The first step in functionalizing the sensor involves activating its surface. This was achieved via a piranha treatment. A piranha solution consisting of a 3:1 ratio of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) was prepared. The sensing (NCF) end of the fabricated sensor was immersed into the piranha solution for duration of 30

minutes. After 30 minutes, the sensing end was removed from the piranha solution and left to air dry for 10 minutes before being rinsed with DI water to hydroxylate the sensor surface.

The second step in functionalizing the sensor involves performing a silane treatment. After the sensor was hydroxylated via piranha treatment, it was treated with the silane coupling agent (3-aminopropyl) triethoxysilane (APTES). To carry out the silane treatment, the activated sensor surface was immersed in a solution of APTES for a period of 30 minutes. Subsequently, the sensing region was left to air dry for 10 minutes.

The third and final step of the functionalization process involved the immobilization of the ligand Meso-Tetra(4-carboxyphenyl)porphine ($C_{48}H_{30}N_4O_8$) onto the surface of the silanized sensor. The sensing (NCF) end of the sensor was dipped into a solution of Meso-Tetra(4-carboxyphenyl)porphine for 15 minutes. The sensor was then removed from the solution and allowed to air dry for 5 minutes before being immersed into the solution once again. This completed 1 cycle. This procedure was repeated for a total of four cycles. After the fourth cycle, the sensor was allowed to air dry for 2 hours.

3. SENSOR CALIBRATION

The calibration of the bare NCF sensor was conducted using solutions of varying refractive index (RI) values. The sensing setup schematic is shown in Fig. 1. The fabricated sensor was interrogated using the broadband light source connected via a three-port circulator and its reflectance spectrum was measured and recorded using the Optical Spectrum Analyzer (OSA). Light from the light source is coupled into port 1 of the circulator and the reflected light from the sensor head is coupled to port 3 of the circulator which is connected to the OSA.

Figure 1. Sensing Schematic and (inset) Sensor configuration

The sensor operates on the basis of the principle of Multi Mode Interference (MMI), which can be explained as follows: As light propagates along the SMF and enters the multi mode region of the NCF, the higher order modes get excited due to the mode field mismatch and an interference occurs between the different modes as the beam travels through the NCF^[3]. The coupling efficiency between the back reflected field, as a result of Fresnel reflection in the NCF and the fundamental mode in the input SMF is dependent on parameters such as the length of the NCF section, wavelength and refractive index of the surrounding medium^[4].

The formation self-images as a result of the interference pattern produced in the NCF section is governed by the following equation^[5]:

$$\lambda_{dip} = p \left(\frac{n_{mmf} W_{mmf}^2}{L} \right) \quad p=0,1,2,3\dots \quad (1)$$

where, λ_{dip} denotes the wavelength of spectral dip, p is the self image number, n_{mmf} is the effective refractive index of the NCF, W_{mmf} is the effective diameter of the NCF and L denotes the length of the NCF. From the Equation (1) it is apparent that λ_{dip} shifts to longer wavelengths when the effective refractive index increases.

The sensor was immersed into different RI solutions and the spectrum was monitored by using OSA. The spectral response of the sensor is presented in Fig. 2 (insets). It is observed that with increasing RI, λ_{dip} shows a red shift which is in accordance with Equation (1). Dip shift vs RI plot is presented in Fig. 2. It is observed that the sensor exhibits a very good sensitivity to RI changes and the response displays a good fit to a 2nd degree polynomial ($R^2 = 0.9888$).

Figure 2. Sensor RI calibration curve and (insets) Sensor RI spectral responses

4. RESULTS AND DISCUSSION

In order to test the functionalized sensor's response to nickel ions, the functionalized sensor was exposed to Ni^{2+} solutions in the concentration range of 0.001mM to 1mM prepared by dissolving Nickel Chloride ($NiCl_2$) in DI water and the spectrum was recorded in the OSA. From Fig. 3(inset), it is observed that the interference dips of the reflectance spectrum shifts towards longer wavelengths with increasing nickel ion concentration. The ligand Meso-Tetra(4-carboxyphenyl)porphine ($C_{48}H_{30}N_4O_8$) is an aza, cyclic molecule with electron rich interior cavities within which the heavy metal ion is encapsulated via ion - dipole interactions. This can be explained on the basis that the two-pyrroline nitrogens have the ability to accept two protons while the two $-NH$ groups are capable of losing an equal number of protons^[6]. As a result of the binding of nickel ions present in the solution to the electron rich interior cavity of the ligand there is a change in the ambient RI around the NCF interface, which causes the interference dips to shift. The plot of sensor dip shift with change in Ni^{2+} concentration is presented in Fig. 3. It is observed that the sensor exhibits a linear response ($R^2 = 0.8411$) in the range up to 0.02mM with a Ni^{2+} detection sensitivity of 121.03 nm/mM.

Figure 3. Dip shift vs Ni^{2+} concentration and (inset) Sensor spectral response to Ni^{2+} concentrations

5. CONCLUSION

A novel fiber optic intermodal sensor for detection of Ni^{2+} ions has been demonstrated. A very specific ligand to Ni^{2+} , Meso-Tetra(4-carboxyphenyl)porphine ($\text{C}_{48}\text{H}_{30}\text{N}_4\text{O}_8$) is directly immobilized onto the NCF sensor through covalent bonding and acts as binding sites for Ni^{2+} ions. Sensitivity of the sensor to Ni^{2+} ions was evaluated to be 121.03 nm/mM and the sensor is a viable alternative to polymer based fiber optic heavy metal ion sensors.

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