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Heavy Metal Cation Probe with Signal to Noise Ratio Measurement of Fiber Bragg Grating

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Abstract

An intensity-modulated Nickel ions (Ni^{2+}) probe is experimentally demonstrated by using optical fiber Bragg grating (FBG) cascaded by a cleaved fiber end which is functionalized by multilayers of chitosan/poly acrylic acid (PAA). The multilayer film can effectively adsorbed Ni^{2+} that modulate signal to noise ratio (SNR) of the FBG. The proposed probe exhibits an enhanced sensitivity with detection limitation of 0.01 mM. This kind of relative measurement method contributes to eliminate power fluctuation of the optical source. Temperature can be monitored simultaneously by wavelength shift, which is benefit to minimize temperature cross effect on Ni^{2+} detection in the future.

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Keywords: Fiber Bragg grating; Heavy metal detection; Optic fiber sensor.

1. Introduction

Heavy metal (e.g. Hg, Pb, Ni, Zn, As) detection in water-quality monitoring systems has been widely required because certain metal cation attributed to the allergy, carcinogenic effect and even cancer to human being. Traditional detection techniques for heavy metal need sophisticated pre-processing or equipment like atomic

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absorption spectroscopy [1]. Recently, fiber optical sensors have attracted a lot of attentions, since they possess many advantages such as electrically passive operation, compact and cost effective that are quite qualified in detecting where samples happen to be located [2]. Besides, intensive investigations using hydrogel have been demonstrated on absorption of heavy metal ions from water like chitosan, poly acrylic acid (PAA) and polyvinyl alcohol (PVA) [3-6]. And these kinds of hydrogel have many useful physical capture effect caused by the presence of cation, which caused swelling and refractive index variation [7]. PVA/PAA hydrogel coated on Mach-Zehnder fiber interferometer has been realized for detecting the Nickel ions (Ni^{2+}) at the limitation of 0.01 mM [8]. However, the achieved heavy metal detecting sensor formed by a section of photonic crystal fiber, operated in transmission mode and demodulated by dip wavelength shift that may cause inconvenience in practical application.

In this work, an intensity-modulated Ni^{2+} probe is experimentally demonstrated by using fiber Bragg grating (FBG) with cleaved end face which is functionalized with the chitosan and PAA. The chitosan/PAA multilayer film at the fiber end can effectively adsorb Ni^{2+}, which modulates the background intensity of the FBG rather than the peak intensity. Therefore, the concentration of Ni^{2+} can be measured by detecting signal to noise ratio (SNR) of the FBG. The relative measurement method can not only eliminate the error caused by power fluctuation of the optical source, temperature but also can be simultaneously measured by monitoring peak wavelength shift of the FBG, which is benefit to further compensate the cross effect on the Ni^{2+} detection.

2. Sensor Fabrication and Principle

The inset of Fig. 1 illustrates the detailed structure of the proposed sensor, which was formed by a normal FBG written in a hydrogen-loaded single-mode fiber (CORNING, SMF-28) with a Bragg reflection wavelength of 1558.47 nm at room temperature, reflectivity of 14 dB and 3-dB bandwidth of 0.2 nm. The fiber length between the FBG and a cleaved fiber end is ~3 cm. The fiber end was firstly immersed in the piranha solution (sulfuric acid, H_2SO_4 and hydrogen peroxide, H_2O_2 in the volume ratio of 3:1) for 60 minutes and rinsed thoroughly with deionized water (DI water) before drying under the purified nitrogen gas. After that, the fiber surface was removed any organic residue and hydroxylated. The multilayer film used consists of chitosan (polycation) and PAA (polyanion). Chitosan solution with the concentration of 2% was prepared by dissolving chitosan powder in 4% acetic acid. PAA solution with the concentration of 8% was prepared in Milli-Q water (Millpore). The solutions were stirred continuously for at least 12 hours at 80ºC and filtered to remove any undissolved materials. The cleaned fiber end was coated layer by layer (LBL) via free radical initiated polymerization from the monomeric form due to the property of molecular structure in dip coating process with chitosan and PAA solution alternately. After every step, the fiber end was immersed in DI water to remove any excess materials to make the multilayer uniform. Eleven bilayer chitosan/PAA multilayer film was coated on the fiber end, the Fresnel reflectivity R_F of which can be described by [9]:

$$R_F = \left(\frac{n_f - n_m}{n_f + n_m} \right)^2 \tag{1}$$

where n_f, n_m is refractive index of the fiber core and the chitosan/PAA multilayer film, respectively. The reflective SNR (with unit of dB) of the FBG can be expressed by [9]:

$$\Delta R = 10 \lg \left[\frac{R_{FBG}}{R_F} \right] \tag{2}$$

where R_{FBG} is reflectivity of the FBG at the Bragg wavelength, which is not induced by the surrounding refractive index.

The enhanced affinity of chelating ligands (i.e., amine) of the chitosan /PAA multilayer film captures the metal ion (i.e., Ni^{2+}), which is so called the Chelate Effect. When the Ni^{2+} was adsorbed by the chitosan/PAA multilayer film in the solution, the reflective index of the multilayer film will increase and hence the SNR of the spectrum will thereupon change based on Eqs. (1) and (2). Therefore, we can inversely calculated out the concentration of the Ni^{2+} by the experimental data of SNR.

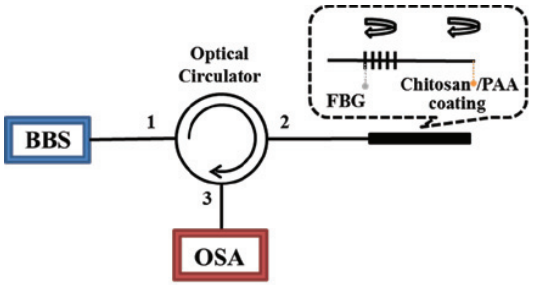

Fig. 1 Experimental setup for heavy metal detection.

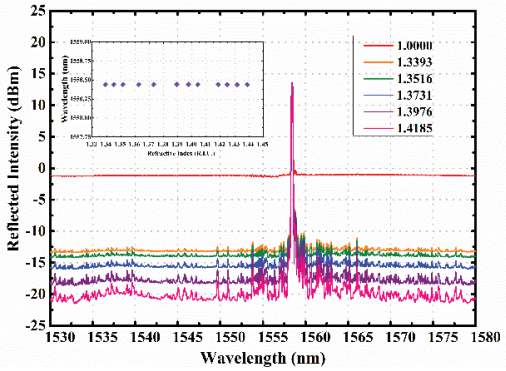

Fig. 2 Reflected spectra of refractive index response.

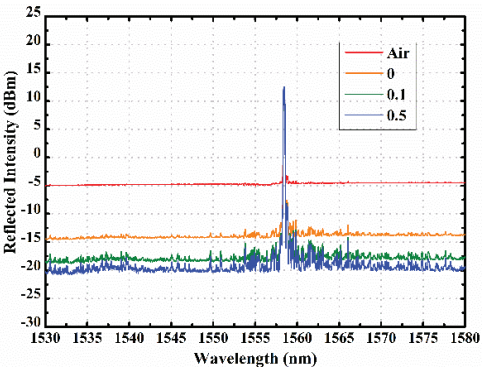

Fig. 3 Reflected spectra of heavy metal detection.

Furthermore, the Bragg reflection wavelength of FBG is sensitive to environmental temperature but insensitive to surrounding refractive index. Simultaneous measurement of Ni^{2+} concentration and temperature is possible by measuring SNR and Bragg reflection wavelength of FBG at the same time.

3. Experimental Results and Discussions

The experimental setup is shown in Fig.1, which contains a broadband light source (BBS), an optical circulator (OC), an optical spectrum analyzer (OSA, Yokogawa AQ6370), and the proposed Ni^{2+} fiber probe. The light from BBS launched into the fiber probe through the OC. The reflected light is guided into the OSA for measurement of reflected spectrum.

In the experiment, we tested the response of the bared fiber end without coating to the refractive index firstly by using glycerin-water solutions in different ratio. The measurement results are shown in Fig. 2. Both intensity and wavelength of the FBG reflection are nearly not changed except the Fresnel reflection intensity (the bottom of the spectrum) decreased gradually with refractive index. This agrees well with the theoretical prediction. There are some minor peaks appearing beside the Bragg reflection peak of the FBG in the reflection spectra when the fiber end is surrounded by the refractive index liquid. They are very weak side reflection modes of the FBG, totally covered by the Fresnel reflection when the probe is in the air (i.e. refractive index equals to 1.000).

Then we tested the fiber probe functionalized with the chitosan/PAA multilayer film with varying concentrations of $NiCl_2$ in pH 6.7 2-(N-morpholino) ethane sulfonic acid buffer with 150 mM of sodium chloride added to keep ionic concentration relatively constant. The measured reflection spectra when the proposed probe was in the air and immersed into the solution with the concentrations of Ni^{2+} are 0 (i.e. buffer), 0.1, 0.5 mM are shown in Fig. 3. It can be seen that the intensity of Fresnel reflection decrease with the concentrations of Ni^{2+}, which means that refractive index of the multilayer film increases with the presentation of Ni^{2+}. In addition, intensity and wavelength of the FBG peak reflection keep nearly stable.

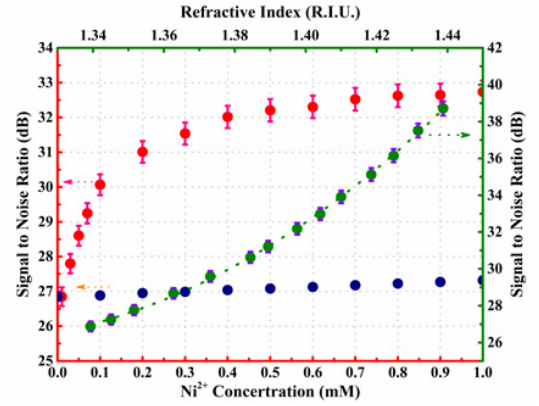

Fig. 4. SNR of FBG versus refractive index and Ni^{2+} concentration.

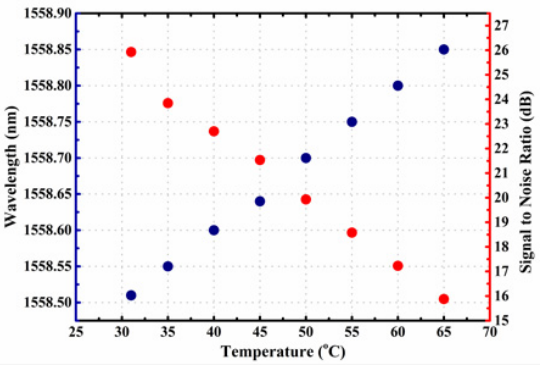

Fig. 5. The Bragg wavelength and SNR versus temperature.

From the measured reflection spectra, it can be seen that the SNR of the FBG increases gradually with the concentrations of Ni^{2+}. In order to eliminate the influence of FBG side modes and random noise of the reflection background, we chose the reflection intensity at the right side of the FBG reflection peak from 1540 to 1550 nm, and figured out the SNR based on the averaged value and the Bragg reflectivity. Figure 4 shows the achieved SNR against concentrations of Ni^{2+}. The SNR increased from 26.71 dB to 32.86 dB when the concentrations of Ni^{2+} increased from 0 to 1mM. The deviation ranges achieved from multiple measurements are indicated in Fig. 4.

We also measured SNR of the fiber probe versus refractive index. The results are shown in Fig. 4. By data fitting, the quadratic function is $y = 684.1x^2-1782.8x+1187.6$ with x, y corresponding to refractive index and SNR of the FBG reflection spectrum, respectively. Based on this, variation in refractive index of the multilayer film is up to ~0.07, which is quite larger than 0.005 the refractive index variation with the concentration from 0 mM (i.e. buffer solution) to 1mM Ni^{2+} solution tested by the bared fiber end. Therefore, the differential refractive index of various Ni^{2+} concentrations can be enhanced by the presence of the chitosan/PAA multilayer film. The effect of Ni^{2+}absorption by chitosan/PAA contributes to the variation on the fiber end the SNR of FBG, which enhanced the measurement sensitivity in our proposed fiber probe.

For temperature measurement, we put the fiber probe in a temperature-controlled chamber and changed temperature from 30ºC to 65ºC (without Ni^{2+} solution), and recorded Bragg wavelength shift of the FBG and SNR. The measurement results, as shown in Fig. 5, indicate that independent temperature measurement can be achieved from Bragg wavelength shift of the FBG with temperature sensitivity of 10 pm/ºC because the concentrations of Ni^{2+} solution doesn't affect Bragg wavelength of the FBG. But SNR of the FBG, as shown in Fig. 5 as well, decreases with temperature. This is caused by the temperature-induced expansion of the multilayer film. Therefore, temperature compensation scheme should be required to achieve temperature-independent measurement. It will be further studied in future work.

4. Conclusion

The intensity-modulated Ni^{2+} fiber probe has been experimentally demonstrated by using chitosan/PAA functionalized fiber probe. From the experiment, Ni^{2+} can be effectively adsorbed onto the chitosan/PAA multilayers film at the fiber end and modulate the SNR of the FBG. Therefore, Nickel ions detection is realized with detection limitation of 0.01 mM. This relative measurement method not only allows elimination of noise due to intensity fluctuation of the optical source, but also temperature can be monitored simultaneously to minimize temperature cross effect on Ni^{2+} detection.

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