

Study on pH Sensor using Methylene Blue Adsorption and A Long-Period Optical Fiber Grating Pair

Younghee Jeon, Jaejoong Kwon, and Byoungho Lee*

School of Electrical Engineering, Seoul National University Kwanak-Gu Shinlim-Dong, Seoul 151-744, KOREA

(Received March 10, 2006 : revised March 10, 2006)

We propose a new pH-sensing scheme using a methylene blue adsorption on an optical fiber cladding surface. Interactions between the silica and hydroxyl ions of a base solution induce the surface of the silica negatively charged. The charged surface attracts the positively charged chromophores of methylene blue. As the pH of the solution is reduced, the electrostatic attraction will also be reduced. This electrostatic attraction can change the transmitted light intensity of the cladding mode, since the boundary condition changes. We also carried out a simulation to verify the effect from external refractive index change around a long-period fiber grating. Our results confirm that the wavelength shift by external refractive index change is negligible compared to the transmitted light intensity variation of the cladding mode. By using a long-period grating pair, we can detect the cladding mode transmittance variations. Experimentally, we showed the possibility of pH sensing in the 1.5 μm infrared region.

OCIS codes : 050.0050, 060.0060, 060.2370

I. INTRODUCTION

Accurate measurement of pH is required in diverse fields, such as the chemical industry, medicine and the environmental monitoring, and hence it has been a challenging research topic. Among the several candidates, the pH sensor using an optical fiber has many advantages compared with conventional (potentiometric) pH sensors. For instance, immunity to electromagnetic interference, intrinsic safety, possibility of miniaturization, and bio-compatibility make an optical fiber pH sensor suitable for in vivo blood monitoring in electromagnetically noisy environments.

The optical fiber sensors have also certain advantages that include lightweight, small size, high sensitivity, large bandwidth, and ease in implementing multiplexed or distributed sensors [1]. Previously, there were several reports about pH sensing methods using optical fibers. Some reported on the evolution of a fluorimetric and fluorescence intensity [2] or decay time [3], and pH indicators. But, these sensors have inherent limitations. The range over which the output is linear is very limited and the cost of techniques could also be very high due to the price of UV optics needed for fluorimetric work as well as the complication of immobilizing the indicator in a polymer by the sol-gel method [4] or self-assembly

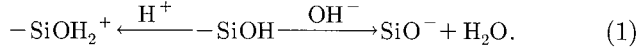
method [5]. Among them one used the property of chemical interaction between an optical fiber and methylene blue (OH⁻ indicator, dye) [6]. When the surface of silica contacts with the pH solution, the surface becomes electrically charged. If it becomes negatively charged, it attracts positively charged chromophores of methylene blue. The adsorbed methylene blue absorbs the evanescent field of visible light in the optical fiber. And recently a method using the evanescent field of a side-polished optical fiber has been reported [7]. However, in the previous works [6,7], for the exposure of evanescent field, deep etching or polishing in the middle or end region of the fiber was required. But, these additional processes physically weaken the optical fiber.

In this paper, we propose a new pH-sensing scheme without the deep etching process. The proposed method uses a pair of long-period optical fiber gratings (LPGs), which involve the cladding modes. We will show the possibility of pH sensing in the 1.5 μm infrared region. In the second section we will discuss the theories about chemical interaction and light propagation in LPGs. Then, in the third section we will discuss our experimental and simulation results. The last section shows the conclusion of our research.

II. THEORIES

2.1 Theory of chemical interaction

In an acid or base solution, the surface of optical fiber that contacts the test solution becomes charged by H^+ or OH^- ions. These chemical interactions are expressed as Eq. (1) [6]:



For example, in the pH 3 solution the surface of silica optical fiber becomes positively charged. On the other hand, it becomes negatively charged in the pH 9 solution. In those aqueous solutions, the chromophores of methylene blue ($C_{16}H_{18}N_3SCl \cdot 3H_2O$, F.W. 373.89) become positively charged because they must indicate hydroxyl ions in solution. Hence the addition of methylene blue to pH solution that contains an optical fiber induces adsorption or rejection of chromophores. This principle can be understood from the chemical structure of methylene blue. Fig. 1 shows the explicit molecule structure. As shown in Fig. 1, methylene blue is originally neutrally charged, but in aqueous solution methylene blue molecules get hydrogen ions from H_2O . So, the processes involved are reduction and oxidation. In previous works [6,7] using optical fiber, the transmitted visible light wavelength becomes changed by absorption of adsorbed methylene blue. This absorption process is

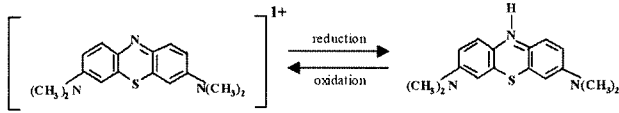


FIG. 1. Chemical structure and chemical reaction of methylene blue.

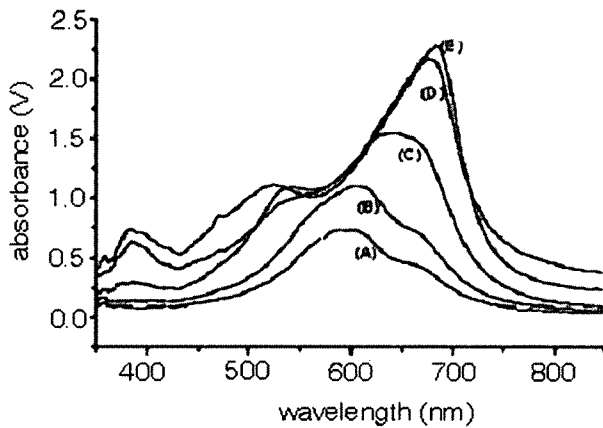


FIG. 2. Absorption spectrum of methylene blue (1 mM) at a 2-cm^2 ITO-coated glass waveguide working electrode. The spectra measured at (a) 0.0 V; (b) -0.1 V; (c) -0.2 V; (d) -0.3 V; (e) -0.6 V

associated with the chemical bonding structure. All molecules undergo continual rotations and vibrations. Each of these motions has its own natural frequency, which is based on the type of motion, the masses of the atoms, and the strengths of the bonds between them. Thus, each kind of bond has a characteristic range of absorption wavelengths, and the exact wavelength and amount of IR radiation absorbed by a given bond depend on the overall structure of the molecule. A methyl group may be identified with C-H absorption at 1380 cm^{-1} ($7.2464\text{ }\mu\text{m}$). As shown in Fig. 2 [8], the absorption spectrum of methylene blue is located around 600 nm. Since methylene blue mainly absorbs visible light, in our monitoring wavelength near $1.5\text{ }\mu\text{m}$ it cannot be observed.

In the case in which chromophores attach on the surface of optical fiber in pH solution, conditions at the boundary between cladding and the surroundings also undergo a change. Added methylene blue causes variation of the external refractive index and surface condition.

2.2 Theory of long-period fiber gratings

We use a pair of LPGs to measure the change in transmitted light intensity of a cladding mode along the fiber. The higher order mode of LPG is highly sensitive to the surroundings, which are temperature, strain and refractive index variations [9]. Eqs. (2)-(4) [9] show relation between resonance wavelength and the other physical parameters.

$$\begin{aligned} \frac{d\lambda_{res}}{dT} &= \lambda_{res} \cdot \gamma \cdot (\alpha + \Sigma_{temp}) \\ \frac{d\lambda_{res}}{d\varepsilon} &= \lambda_{res} \cdot \gamma \cdot (1 + \Sigma_{strain}) \end{aligned} \quad (2)$$

$$\begin{aligned} \frac{dn_{ext}}{d\lambda_{res}} &= \frac{d\lambda_{res}}{d\Lambda} \\ \gamma &= \frac{d\lambda_{res}/d\Lambda}{n_{co}^{eff} - n_{cl,v}^{eff}} \end{aligned} \quad (3)$$

where α is the thermal expansion coefficient of the fiber and γ describes the waveguide dispersion, and

$$\begin{aligned} \Sigma_{temp} &= \frac{\zeta_{co} n_{co}^{eff} - \zeta_{cl} n_{cl,v}^{eff}}{n_{co}^{eff} - n_{cl,v}^{eff}} \\ \Sigma_{strain} &= \frac{\chi_{co} n_{co}^{eff} - \chi_{cl} n_{cl,v}^{eff}}{n_{co}^{eff} - n_{cl,v}^{eff}} \\ \Sigma_{ext} &= \frac{u_v^2 \lambda_{res}^3 n_{ext}}{8\pi^3 (n_{co}^{eff} - n_{cl,v}^{eff})(n_{cl}^2 - n_{ext}^2)^{3/2}} \end{aligned} \quad (4)$$

where Σ_{temp} , Σ_{strain} and Σ_{ext} describe the temperature, strain and external refractive index dependences. ζ and

χ are the thermo-optic and elasto-optic coefficients and u_w is the w th root of the zeroth-order Bessel function of the first kind.

A pair of LPGs constitutes a Mach-Zehnder interferometer (MZI) that has two optical path lengths as the core mode (fundamental mode) and a cladding mode, hence its specific interference pattern comes out as the spectral fringe pattern [10].

As mentioned in section 2.1, the addition of methylene blue induces surface condition and refractive index changes in pH solution, in other words the external environment of silica becomes changed. At the boundary of the silica surface the evanescent field, the tail of the cladding mode, is sensitive to the external environment. Adsorbed methylene blue operates like dielectric film, so that it induces variation of the evanescent field in a propagating cladding mode. We can regard this effect as the enhanced Fresnel reflection. On the other side, the external refractive index variation results in the change of effective refractive index. So, that is able to make a change of resonance wavelength and light transmission of LPG. But we will verify, by simulation in section 3.2, that the wavelength shift is a very small quantity compared to transmission changes. Therefore, if we measure the transmitted light intensity with a fixed wavelength of a cladding mode, we can get information enough to figure out the pH concentration of different solutions. Fig. 3 shows the conceptual configuration in the acid case and the base case of the pH solution. Consequently the spectral fringe pattern at the output changes according to the pH value.

III. EXPERIMENT AND SIMULATION

3.1 Experimental results

We used LPGs fabricated by an amplitude mask of

500 μm pitch. The spacing of the LPG pair was 50 cm and grating length was 3 cm. To get the definite effect of the cladding mode we used slightly etched fibers. The pH solution tank has a diameter of 10 cm and capacity of 60 ml. Measuring range is from pH 3 to pH 9 and methylene blue concentration is varied from 0 mmol/l to 0.81 mmol/l. In the higher concentration of methylene blue, the variation of transmittance is saturated. The schematic of the experimental setup is shown in Fig. 4. The experimental results are shown from Fig. 5 to Fig. 7. They show the changes of transmitted light intensity with addition of the methylene blue in the solution of pH 3 and pH 9 near 1548 nm. As shown in Fig. 5 and Fig. 6, the transmitted light intensity with the increment of methylene blue concentration becomes larger, commonly. In the case of pH 4 solution, the changed value is from 0.018 to 0.032 dB along the methylene blue concentration of 0.27 to 0.81 mmol/l, but in the case of pH 9 the increasing quantities corresponding to the higher concentration become larger than the case of pH 4 solution, from 0.052 to 0.124 dB. So the effect of the enhanced Fresnel reflection results in more guiding of evanescent field in cladding mode and in the basic solution this effect appears definitely. Fig. 7 shows the transmittance variation for each solution (from pH 3 to pH 9) when the concentration of methylene blue increases.

Under the assumption that the addition of dye causes the external refractive index changes, we will examine the spectral changes throughout the simulation. The effective refractive index variation by the variation of the external refractive index changes a resonant wavelength and transmitted light intensity of the fringes. However, in experimental results the wavelength shift of the fringe pattern was so small that we cannot discriminate it, whereas the change of transmitted intensity is easily seen.

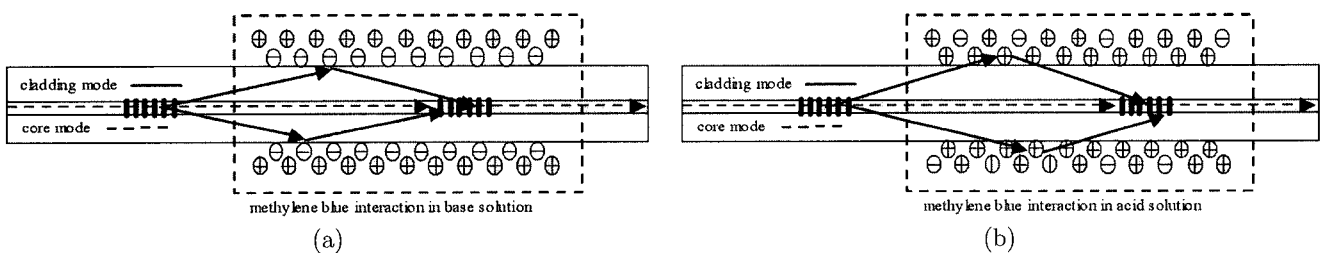


FIG. 3. Conceptual configuration of the proposed pH sensor (a) In base solution, (b) in acid solution

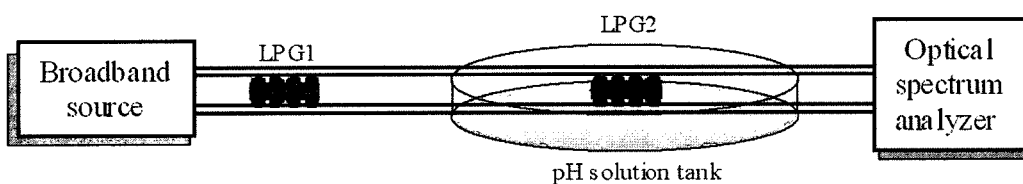


FIG. 4. Schematic of the experimental setup.

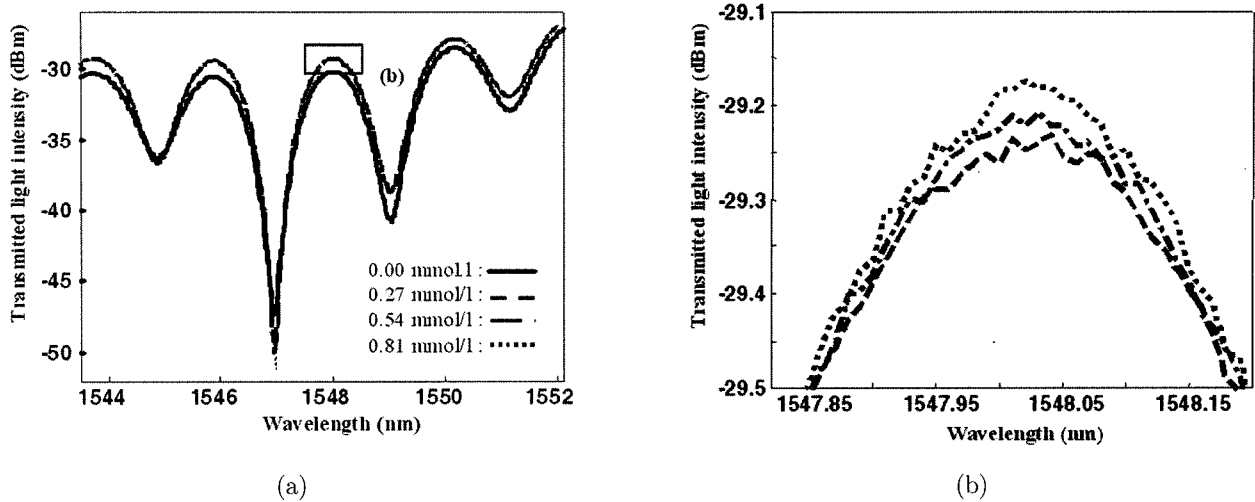


FIG. 5. (a) Transmitted light intensity in pH 4 with methylene blue variation and (b) the enlarged spectra of the inset.

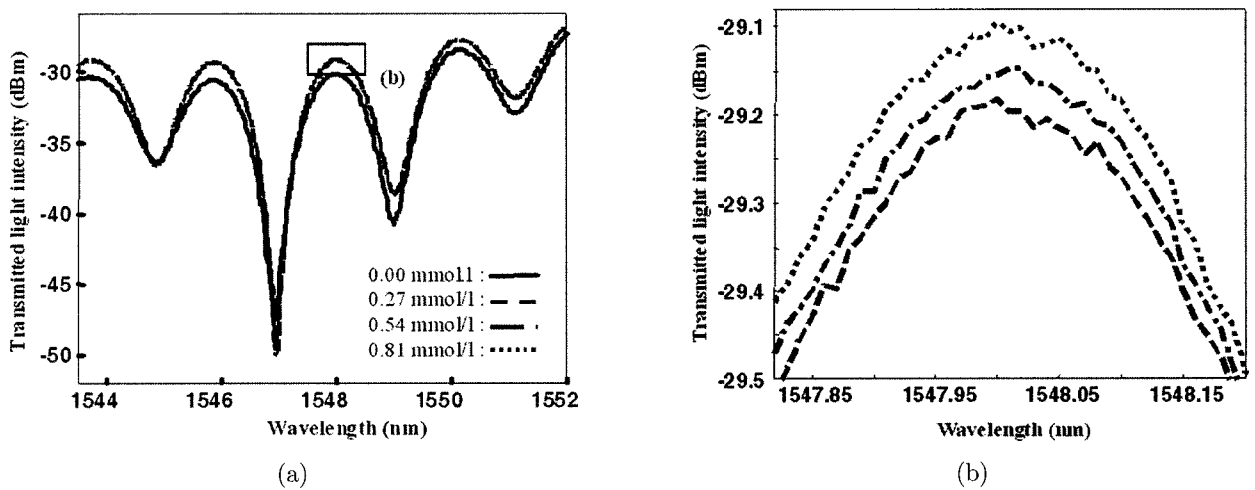


FIG. 6. (a) Transmitted light intensity in pH 9 with methylene blue variation and (b) the enlarged spectra of the inset.

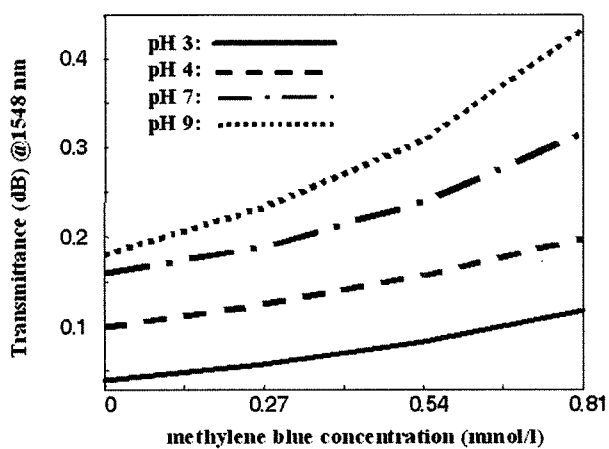


FIG. 7. Changes of the transmitted light intensity with the variations of methylene blue concentration and pH concentration

3.2. Simulation results

For the more exact analysis of the experimental result, we should consider the effect of external refractive index change in pH solution with addition of methylene blue. From the theoretical estimation, the transmitted light intensity and resonance wavelength of the fringe of LPG pair should be changed according to the changed effective refractive index. There are several previous researches about this detailed discussion [11]. For a supplementary verification we carried out simulation of the effect of external refractive index change to LPG pair spectrum. Fig. 8 shows the changes of fringe pattern of the LPG pair. Simulation parameters are the same as experimental parameters except for the two assumptions. The LPG pair is composed of exactly the same LPGs and has no propagation loss. Simulation algorithm is implemented by using discretized coupled-

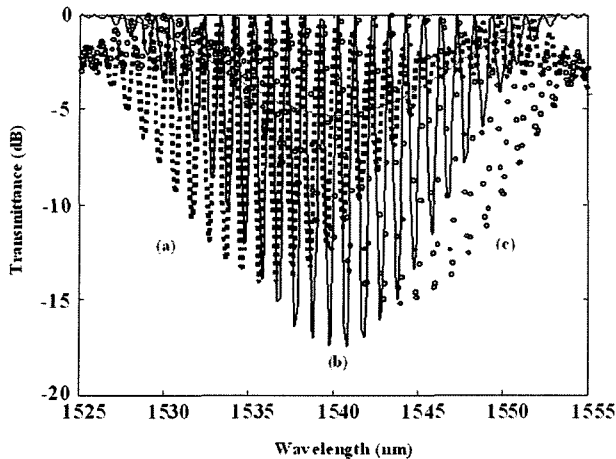


FIG. 8. Fringe pattern changes of LPG pair according to the next variations (a) left (dashed) is $\Delta n_{\text{ext}} = -8 \cdot 10^{-5}$, (b) center (solid) is and $\Delta n_{\text{ext}} = 0$ (c) right (dashed dot) is $\Delta n_{\text{ext}} = +8 \cdot 10^{-5}$

mode theory [12].

As shown in Fig. 8, the shift of wavelength is negligible compared to the transmitted light intensity change. Hence we confirm that under the tiny refractive index variation the dominant phenomenon is the variation of the transmitted light intensity. Not only for the simulated estimation, but for the experimental results, the transmitted light intensity variation along with the increasing pH values is dominant. On the bases of this mechanism, we can ascertain that cohesive interaction on the surface of optical fiber causes reinforcement of the cladding mode guiding.

IV. CONCLUSION

As we already mentioned, we proposed a new scheme for pH sensing using an LPG pair without deep etching process. Our experimental result showed the possibility to measure pH values using a pair of LPGs in the 1.5 μm infrared region differently from previous works. This sensing scheme is useful compared to previous works using single mode optical fiber because the transmission loss of conventional single mode fiber is minimum at around 1.5 μm . And we also carried out simulation for the effect of external refractive index change around long-period fiber gratings by addition of methylene blue. From the experimental result, we can get the sensitivity 0.0184 dB/pH. But the variation of the transmitted light intensity is so small that it requires a supplementary technique such as amplification for precise measurement. And additional experiment using a different pH

indicator in the acid region increases the sensing range and the sensitivity. Throughout these improvements, we expect it is possible to get more accurate results.

*Corresponding author : byoungcho@snu.ac.kr

REFERENCES

- [1] B. Lee, "Review of the present status of optical fiber sensors," *Optical Fiber Technology*, vol. 9, pp. 57-59, 2003.
- [2] A. M. Rollins, Z. Xu, R. Alcla, and J. A. Izatt, "A novel wide range single fiber optic fluorescence pH sensor," *Summaries of Papers Presented at the Conference on CLEO '97*, vol. 11, pp. 187, 1997.
- [3] S. Draxler and M. E. Lippitsch, "Optical pH sensors using fluorescence decay time," *Sensors and Actuators B*, vol. 11, pp. 421-424, 1993.
- [4] J. Y. Ding, M. R. Shahriari, and G. H. Sigel, "Fibre optic pH sensors prepared by sol-gel immobilization technique," *Electronics Letters*, vol. 3, pp. 1560-1562, 1991.
- [5] F. J. Arregui, I. Latasa, and I. R. Matias, "An optical fiber pH sensor based on the electrostatic self-assembly method," *2003. Proceedings of IEEE Sensors*, vol. 1, pp. 107-110, 2003.
- [6] B. J.-C. Deboux, E. Lewis, P. J. Scully, and R. Edwards, "A novel technique for optical fiber pH sensing based on methylene blue adsorption," *Journal of Lightwave Technology*, vol. 13, pp. 1407-1414, 1995.
- [7] A. Gaston, I. Lozano, F. Perez, F. Auza, and J. Sevilla, "Evanescence wave optical-fiber sensing (temperature, relative humidity, and pH sensors)," *IEEE Sensors Journal*, vol. 3, pp. 806-811, 2003.
- [8] N. Matsuda, J. H. Santos, A. Takatsu, and K. Kato, "In situ observation of absorption spectra and adsorbed species of methylene blue on indium-tin-oxide electrode by slab optical waveguide spectroscopy," *Thin Solid Films*, vol. 445, pp. 313-316, 2003.
- [9] X. Shu, L. Zhang, and I. Bennion, "Sensitivity characteristics of long-period fiber gratings," *Journal of Lightwave Technology*, vol. 20, pp. 255-266, 2002.
- [10] E. M. Dianov, S. A. Vasiliev, A. S. Kurkov, O. I. Medvedkov, and V. N. Protopopov, "In-fiber Mach-Zehnder interferometer based on a pair of long-period gratings," *22nd European Conference on Optical Communication - ECOC '96*, pp. 65-68, 1996.
- [11] H. J. Patrick, A. D. Kersey, and F. Bucholtz, "Analysis of the response of long period fiber gratings to external index of refraction," *Journal of Lightwave Technology*, vol. 16, pp. 1606-1611, 1998.
- [12] Y. Jeong and B. Lee, "Nonlinear property analysis of long-period fiber gratings using discretized coupled-mode theory," *IEEE Journal of Quantum Electronics*, vol. 35, pp. 1284-1292, 1999.