Bragg grating chemical sensor with hydrogel as sensitive element

Xiaomei Liu (刘小梅)[1], **Shilie Zheng (郑史烈)**[1], **Xianmin Zhang (章献民)**[1],
Jun Cong (丛 军)[1], **Kangsheng Chen (陈抗生)**[1], **and Jian Xu (徐 坚)**[2]

[1] *Department of Information and Electronic Engineering, Zhejiang University, Hangzhou 310027*
[2] *Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080*

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A novel fiber Bragg grating (FBG) based chemical sensor using hydrogel, a swellable polymer, as sensitive element is demonstrated. The sensing mechanism relies on the shift of Bragg wavelength due to the stress resulted from volume change of sensitive swellable hydrogel responding to the change of external environment. A polyacrylamide hydrogel fiber grating chemical sensor is made, and the experiments on its sensitivity to the salinity are performed. The sensitivity is low due to the less stress from the shrinking or swelling of hydrogels. Reducing the cross diameter of the grating through etching with hydrofluoric acid can greatly improve the sensitivity of the sensor.

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Fiber Bragg grating (FBG) has been extensively used in fiber sensor systems. The sensitivity of FBG to temperature and strain can be employed to measure desired environmental parameters[1−3]. The polymeric hydrogels are crosslinked polymers, which can swell to an equilibrium state in water. The water content depends on the polymer network structure. It can be made responsively with the change of physical structure and chemical properties to the slight change and excitation of external environmental factors, such as temperature, pH, photon irradiation, electricity, pressure, and so on[4−8]. The sensitivity of hydrogel has received great interest in developing novel and smart sensors and controllable switches, etc..

In this letter, we report a novel chemical sensor based on the combination of FBG and hydrogel. The principle of this device relies on the shift of the Bragg wavelength due to volume change of the hygrogel when put in solutions with different salt concentrations. In order to improve the sensitivity of FBG sensor, the diameter of the fiber is thinned by chemical etching so as to increase the shift of Bragg wavelength caused by the stress induced in hydrogel. The sensor for measuring salinity is demonstrated. The primary experiments show that it is potentially used to measure the ion concentration in river, lake, and sea. By modifying the chemical structure of hydrogel, parameters other than salinity can be detected using the same basic approach.

Hydrogels are a range of hydrophilic polymers, which absorb water and swell in aqueous media without dissolution. During the swelling, the volume of the polymer is dilated when the solvent penetrates into the polymer. However this volume dilation induces the crossed polymer molecule links extended in the space, the induced stress results in the shrinkage of the crossed molecule links. When the above two reverse mechanisms balance, the swelling of the hydrogel reaches an equilibrium state. The swelling characteristic of the hydrogel is dependent on the properties of solvent and solute, the pressure and the correlation of the gels. The relation between them can be described by Flory-Huggins's infiltration pressure equation[9]

$$\begin{aligned}\Pi = {} & -RT/V_{\mathrm{c}}[\varphi + \ln(1-\varphi) + \chi\varphi^2] \\ & + VRT[1/2(\varphi/\varphi_0) - (\varphi/\varphi_0)^{1/3}] + RT(N_{\mathrm{gel}} - N_{\mathrm{sol}}),\end{aligned} \qquad (1)$$

where R is the gas constant, T is absolute temperature, V_{c} is the mole volume of the solvent, χ is the correlation parameter of the polymer and the water, φ_0 is the volume fraction of the crossed polymer, φ is the volume fraction of the non-crossed polymer, N_{gel} and N_{sol} are the concentrations of the gel and the ion in the solution, respectively, and V is the amount of the linked polymer per volume when $\varphi = \varphi_0$.

Seen from the Eq. (1), the infiltration pressure comes from the correlation of the polymer molecule link and water, the elasticity of the crossed polymer molecule and the ion concentration difference in and out the hydrogel. Therefore, when the hydrogel is put in the solution with different salinities, its volume will be changed.

The sensor device consists of a FBG coated by hydrogel, as shown in Fig. 1. The FBG is clamped using two organic glass disks whose diameter is 1 cm. When the hydrogel absorbs water, it will swell and produce a mechanical expansion, the disks fixed on the two sides of the FBG are physically stretched, the grating period (Λ) expands and red shift of the Bragg wavelength appears. When the sensor is immersed in salinity solution, the hydrogel will shrink and release the water, the grating period minishes and the blue shift of Bragg wavelength

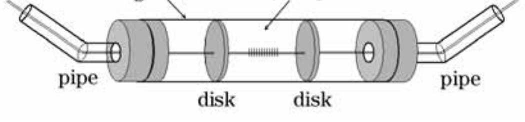

Fig. 1. Polymerization setup of hydrogel and the structure of the hydrogel-coated FBG.

appears. Because of the residual stress induced by the hydrogel is determined by the salinity concentration of the solution, the total shift of the Bragg wavelength is directly related to the salinity concentration of the solution.

When the stress induced by the hydrogel is applied to the optical fiber grating, a resulting shift in the central Bragg wavelength (λ_B) can be approximated by[10]

$$\Delta\lambda/\lambda_B = (1 - P_e)\varepsilon, \tag{2}$$

where ε is the induced strain and P_e is the effective photoelastic constant (≈ 0.22). The stress required to produce a given amount of strain ($\varepsilon = \Delta L/L_0$) in the fiber can be expressed by the simple Hooke's law

$$\sigma = E\varepsilon, \tag{3}$$

where σ is the applied stress and E is the Young's modulus of the glass fiber. As for an etched fiber, the force required to produce a given strain is decreased owing to the reduced cross-sectional area. For example, a force of 0.09 kg can produce a 0.1% strain (1.2-nm shift in the Bragg wavelength) on a FBG, whereas the same force can produce a 1% strain (12-nm shift in the Bragg wavelength) on an etched 40-μm-diameter FBG[11]. It is evident that both the sensitivity of sensor and its tuning range are improved by an etched FBG.

FBG used in the experiment was fabricated by phase-mask method, which has a peak reflectance of 95%, a central wavelength of 1548.8 nm, and a grating length of 1 cm. Two disks were adhered on two ends of the FBG by the cured epoxy, as shown in Fig. 1.

The polyacrylamide hydrogel was prepared by free radical solution polymerization initiated by a photoinitiator. The used monomer is acrylamide (AAm), the cross-linker is $N - N'$ methylene bisacrylamide (MBAAm), and the photoinitiator is α-ketoglutatic acid (KGA). The former two reagents should be recrystallized. These reagents were mixed according to a certain ratio. Before polymerization, the FBG was firstly put in a glass tube as shown in Fig. 2. Then the mixed solution was injected to the tube from the small pipe, and the solution was polymerized under UV irradiation around wavelength of 365 nm.

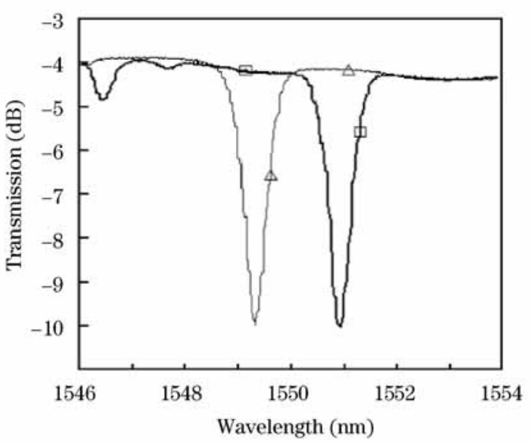

Fig. 2. The transmission spectra of the etched FBG before triangles and after squares hydrogel swelling.

After the hydrogel was polymerized, the sensor was first immersed in the redistilled deionized water. The swelling hydrogel coating pushed the FBG, causing red shift of the Bragg wavelength of the grating. Then the sensor was immersed into a NaCl solution, the shrinkage of the hydrogel caused blue shift of the Bragg wavelength of the FBGs. Different NaCl concentrations corresponded difference of the Bragg wavelength shift.

In order to improve the sensitivity of the sensor device, the FBG was etched with hydrofluoric acid. During etching, the fiber diameter was measured by a microscope. The etching rate was about 1.45 μm/min. After 1-h etching, the diameter of cladding of the fiber grating was removed 37.5 μm. Then the etched FBG was rinsed with methanol. Figure 2 is the transmission spectra of the FBG before and after hydrogel swelling.

The experimental scheme is shown in Fig. 3. The NaCl solutions are with concentration of 0.1−0.7 mol/l. Figure 4 shows the transmission spectra of the sensor versus NaCl concentrations (0.1−0.7 mol/l) with the FBG with and without etching, respectively. The sensing time is 40 min. From Fig. 4, the higher the NaCl concentration of the solution is, the larger the Bragg wavelength of the sensor blue shift gets. It is obvious that blue shifts of

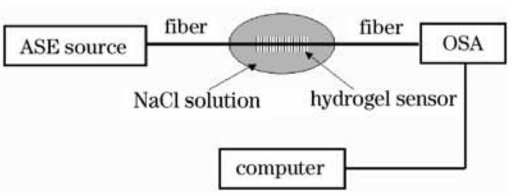

Fig. 3. Experimental scheme of the Bragg grating sensor based on hydrogels.

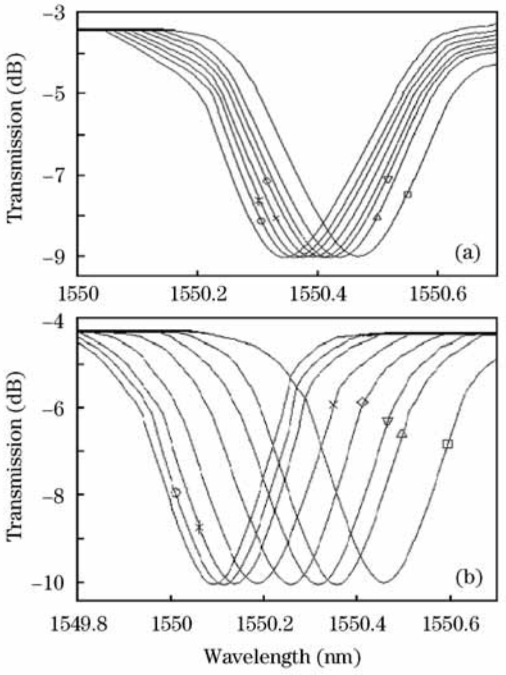

Fig. 4. The transmission spectra of the FBG versus NaCl concentrations with FBG (a) without etching and (b) with etching. The curves from left to right with the NaCl concentrations of 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7 mol/l, respectively.

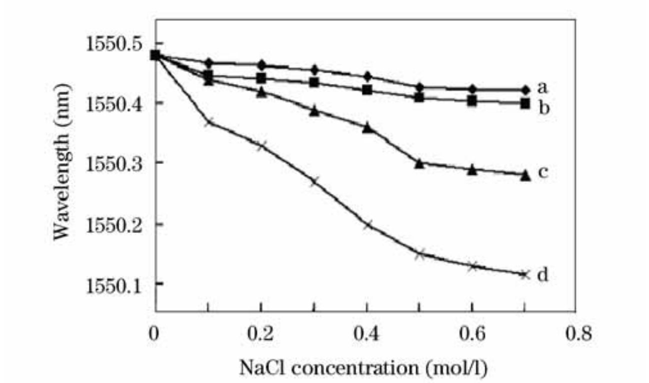

Fig. 5. Bragg wavelengths of the two FBG sensors versus NaCl concentration. (a) Immersed time in 20 min for FBG without etching, (b) in 40 min for FBG without etching, (c) in 20 min for etched FBG, (d) in 40 min for etched FBG.

Bragg wavelength with FBG etching are larger than that without FBG etching. This means an improvement of the sensitivity of sensor. Compared with Fig. 4(b), there is about a 1-dB drop in the overall transmission of the grating in Fig. 4(a). This is possibly caused by light leakage after FBG etching.

Figure 5 shows the Bragg wavelengths shift with different concentrations of NaCl solution. When immersed in NaCl solution, the hydrogel shrinks slowly. When the sensors are immersed in the solution for a longer time (40 min), the responses are improved compared with a shorter time (20 min). After 40 min, the Bragg wavelength of FBG is no longer shift. The sensitivity of sensors can be represented by the slope of the curve in Fig. 5 as $\Delta\lambda_{\mathrm{Bragg}}/\Delta C_{\mathrm{NaCl}}$. It is clear that the slope curves c and d (with etched FBG) are larger than that of curves a and b. The sensitivity of the sensor is improved with the etched FBG. As for the curve d, the best sensitivity of sensor is 0.07 nm/mol/l, which is nearly 8 times larger than that without etching of 0.009 nm/mol/l. However, when the NaCl concentration exceeds 0.5 mol/l, the sensitivity of the device drops. The swelling and shrinkage of the hydrogel are repeatable. In our experiments, one piece of hydrogel is used. After finishing a measurement for a NaCl solution, we put the hydrogel into pure water, the hydrogel can swell to origin state.

In conclusion, a novel FBG salinity sensor has been demonstrated. The sensor employs hydrogel as active element. By reducing the cladding diameter of the FBG through etching, the sensitivity of the sensors is greatly improved. A sensitivity of 0.07 nm/mol/l is obtained which is approximately 8 times larger than that of the FBG without etching. Furthermore, the reflectance of the FBG is not affected after chemical etching. Because of the fact that the swelling and shrinkage of hydrogel not only occur in Na^+ solution, this hydrogel-based sensor can also be designed to sensitive to other ions, such as Ca^{2+}, Mg^{2+} and H^+, etc..

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