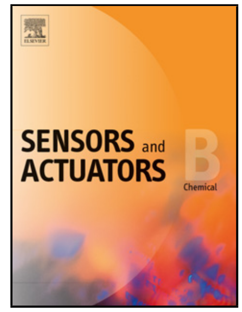


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# Smart Hydrogel-based Optical Fiber SPR Sensor for pH Measurements

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**Highlights**

- A hydrogel-coated optical fiber SPR sensor based on MMF-SMF-MMF structure has been fabricated for pH measurements.
- The experimental sensor is able to indicate pH variations in a wide range of 1 to 12.
- The maximum pH sensitivity of the proposed sensor has reached 13 nm/pH at higher pH region (8~10 pH).

**Abstract:** A hydrogel-coated optical fiber surface plasmon resonance (SPR) sensor based on MMF-SMF-MMF structure has been fabricated for pH measurements. When the solutions with difference pH values contacting the sensing probe, the amount of the dissociated carboxylic ions in the hydrogel will change according to the pH value of the solution. This process will modify the volume and refractive index of the hydrogel, which results in a shift of the SPR wavelength. The experimental sensor is able to indicate pH variations in a wide pH range from1 to 12, and the maximum pH sensitivity of the proposed sensor can reach 13 nm/pH at higher pH region (8~10 pH). The influence of temperature (in the range of 20℃~40℃) on SPR wavelength is found to be weak. Further, the sensor possesses remarkable repeatability and excellent stability. Due to the wide measuring range and simple fabrication process, the sensor is promising to be used for the

pH measurements.

**Keywords:** Surface Plasmon Resonance, pH measurement, smart hydrogel, optical fiber sensor.

## 1. Introduction

In analytical chemistry, environmental monitoring, biochemistry and food safety, pH is a significant physical parameter, which should be monitored in real time [1-4]. Compared with the traditional pH measuring methods, such as acid-base indicator, pH electrode and so on, optical fiber pH sensor has the advantages of easy fabrication, immunity to electromagnetic radiation, biological compatibility and miniature in size [5]. Optical fiber pH sensors can be divided into two categories by utilizing various sensing principles [6]. One category of pH sensors is based on the measurements of absorption and fluorescence of the dyes, owing to biological compatibility, it has been widely used in bio-sensing [3]. The other category bases on coating pH-sensitive materials. Smart hydrogel is one of the popular coating materials, which has been used in optical fiber pH sensors [7-8]. When the pH-sensitive hydrogel contact with the target solution, the amount of the dissociated carboxylic ions in the hydrogel will change according to the pH value of the solution. This process will modify the volume and refractive index of the hydrogel [1,7]. Numerous hydrogel-based optical fiber sensors were investigated, such as photonic crystal fiber (PCF) [9], side-polished D-shaped optical fiber [10], Long-period fiber grating(LPFG) [11] and surface plasmon resonance(SPR) [12]. In 2017, S.K. Mishra et al proposed a hydrogel coated LPFG for pH sensing, the sensitivity of the sensor is 0.66nm/pH over the range from 2 to12 [11]. In 2018, A.L. Aldaba et al reported a polyaniline-coated titled fiber Bragg grating with the measuring range of pH=2 to pH=12 and the maximum sensitivity of 82 pm/pH [7]. As the requirement of pH measurement increasing, the properties of optical fiber sensors, especially sensitivities, are still need to improve. Compared with these sensing structures, optical fiber SPR sensors based on pH-sensitivity hydrogel offers a unique platform for pH measurements due to the ultra-high sensitivity, fast response and less sample consumption. When the sensitive coating layers contact with the target solution whose pH value is changed, the RI of the hydrogel will change accordingly, which will then cause the shifts of SPR dip in the transmission spectrum. Conventional optical fiber SPR sensors remove the cladding to excite evanescent wave to stimulate SPW propagating along the interface between environment medium and metal film. However, removing cladding may reduce the structural strength of the fiber and lead to poor mechanical behavior [16-20].

In order to solve this problem, a multimode-single-mode-multimode fiber splicing structure (MMF-SMF-MMF) has been adopted. When the light propagates from MMF to the SMF, a portion of the light is coupled from MMF core into SMF cladding. Therefore, it can be stimulated SPW propagating along the interface between cladding layer and metal film. In addition, this work uses chemical deposition to replace traditional chemical vapor technique. This method is easy to realize and reduces the cost of film coating. The hydrogel used in our sensor is mainly synthesized with acrylamide (AAM), N, N'-methylene diacrylamide (BAAM), N, N, N, N-tetramethylethylenediamine (TEMED) and methacrylic acid [9]. The performance of the sensor is investigated in the aspects of sensitivity, reproducibility and stability. It can be proved that the influence of the temperature fluctuation on the measured results is weak in the range of 20℃ to 40℃.

## 2. Principle of SPR

Since the transmission of light in optical fiber is based on total internal reflection (TIR), the SPR principle of prism coupling is suitable for optical fiber. The TIR occurs at the interface between the optical fiber and metal layer, due to the evanescent wave can penetrate through the metal layer, it can be generated the SPW on the interface between metal layer and dielectric layer, when two necessary conditions are satisfied: (1) the evanescent wave propagation constant equals that of the SPW; (2) the polarization of the light must have the component perpendicular to the metal surface, i.e. only p-polarized light (TM polarized) can excite SPW [21-22].

On the dielectric interface, according to electromagnetic properties and relevant boundary conditions, when the incident light experiences total reflection on the interface, the light will penetrate into the dielectric layer. The intensity of evanescent field decays exponentially with the distance $d_p$ perpendicular to the interface, the value of $d_p$ is related to the angle of incidence $\theta$, $n_1$ and $n_2$ represent RI of fiber core and cladding, respectively. The penetration depth can be expressed as Eq. (1):

$$d_p = \frac{\lambda}{2\pi\sqrt{n_1^2 \sin^2\theta - n_2^2}} \qquad (1)$$

Eq. (1) means that different combinations of wavelength and incidence angle that can lead to different penetration depth. The x-component of the wave vector $\beta_x$, which is along the metal surface, can be expressed as Eq. (2). ω and θ represent the angular frequency and angle of the incidence. $\varepsilon_0$ is the dielectric permittivity of the optical fiber.

$$\beta_x = \frac{\omega}{c}\sqrt{\varepsilon_0}\sin\theta \qquad (2)$$

According to the Maxwell equations and relevant boundary conditions, under a fixed wavelength, the SPW has a single well-defined propagation constant that depends only on the permittivity of the metal and its surroundings dielectric. It can be expressed as Eq. (3).

$$\beta_{sp} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_m \varepsilon_s}{\varepsilon_m + \varepsilon_s}} \qquad (3)$$

Where $\varepsilon_m$ and $\varepsilon_s$ represent dielectric permittivity of the metal and the dielectric respectively.

When $\beta_x$ is equal to $\beta_{sp}$, the surface plasma resonance will be excited, so the phase match condition expresses as

$$\beta_x = \beta_{sp} \qquad (4)$$

At the resonance wavelength, this condition is fulfilled, and the transmission dip can be obviously recognized in the reflection spectrum. When the refractive index of the dielectric layer is changed, the resonance wavelength will shift according to the phase match condition. The analysis above indicates the measurement principle of SPR. Because the surface plasmon wave is highly confined near the metal surface, the high sensitivity to refractive index can be achieved by SPR sensors.

## 3. Experiment and Discussion

### 3.1 Process of Hydrogel Synthesis

Chemicals used for synthesizing the smart hydrogel in this work are AAM, BAAM, APS, TEMED and methacrylic acid, in which the APS, BAAM and TEMED are used as initiator, cross-linking reagent and catalyst, respectively [11]. All of the reagents are of analytical grade (purchased from Aladdin Ltd) without further purification.

The synthesis process of the hydrogel in this experiment follows the procedure below:

The AAM and BAAM (19:1) were dissolved in water, whose concentration is 80g/L. A polymerization medium was prepared by mixing 50ml aqueous solution of the AAM and BAAM, 100μL methacrylic acid and 1mL ammonium persulphate (0.1g/L). In order to catalyze the reaction, 300μL TEMED was added in the solution. Polymerization of catalyzed solution should incubate under the anaerobic conditions, and the polymerization process was completed after 2 hours.

## 3.2 Sensor structure and Fabrication

The schematic diagram of the sensing system for pH measurement as shown in Fig.1. (a), which consists of a broadband light source, an optical spectrum spectrometer which can detect the wavelength range of 400 to 1000nm and a part of sensing structure. The scheme of the MMF-SMF-MMF structure with hydrogel is shown in Fig.1. (b). The sensing part was made up of two MMFs (62.5/125μm) and one section of SMF (8/125μm) with the length of 10mm. In order to generate surface plasmon resonance, the surface of the MMF-SMF-MMF structure was coated with a thin sliver film. Reference [15] is described the coating procedure in detail, which should be applicable to fabricate samples with small batches simultaneously with good reproducibility.

The thickness of the sliver is controlled by the different of the concentration of Tollen's reagent and the deposition time. The multi-proportion dilution method by deionized water was applied to the Tollen's reagent. As shown in Fig.2. (a), the transmission spectra for the different dilution rate of Tollen's reagent by fixed five minutes. Considering that the narrow full width at half maximum (FWHM) of the resonance dip is helpful to determine the SPR wavelength and increase the measurement accuracy, the best dilution rate of Tollen's reagent during the coating process was 1:6.

With the same concentration of Tollen's reagent, the transmission spectra for different deposition time were investigated experimentally. From Fig. 2. (b), it can be found that the optimum deposition time is three or four minutes.

In order to test the RI sensing performance of the SPR sensor, the sensing head was immersed into the glucose solution with different refractive index. The glucose solutions have been prepared with different concentrations of 5%, 10%, 15%, 20%, 25%, 30%, 35% and 40%, and the corresponding refractive indices were 1.340, 1.347, 1.355, 1.363, 1.371, 1.380, 1.389 and 1.398.

From Fig.3. (a), it can be found that the resonance wavelength experiences red shift with the RI increased. The sensing characteristic curve for RI measurements as shown in Fig.3. (b). In the Fig.3. (b), the relationship between the resonance wavelength and the refractive index can be fitted by the quadratic curve in Eq. (5), where $\lambda_{es}$ is the resonance wavelength, and n is the value of the RI.

$$\lambda_{es} = 43790 \cdot n^2 - 115900 \cdot n + 77280 \quad (5)$$

The structure of the sensing part was fabricated by inserting a conventional single-mode fiber (8/125μm) between two multimode fibers (62.5/125μm), as shown in Fig.4. (a) and (b). The fiber splicing method is employed to fabricate this structure by using a fiber optic fusion splicer (FITEL S178). The sensing probe was coated with a sliver thin layer by sliver mirror reaction method in Fig.4. (c). Finally, the sensing probe was covered by the hydrogel material as shown in Fig.4. (d) and (e).

### 3.3 pH Measurement Experiment

As a reference, the pH sensitivity of the bare SPR sensor without hydrogel layer was investigated. The transmission spectra were obtained for the pH values from 1 to 12 at 22℃. From Fig.5 (a), it can be found that the resonance wavelength is slight changed with the pH values increased. Considering that the pH value is related to the concentration of ions, as well as the refractive index of the measured solution, the slight wavelength shift can be explained by the refractive index sensing principle of SPR sensors. However, the bare SPR sensor is unlikely to be applied in pH measurement due to the low sensitivity. In addition, with the concentration of the hydrogen (hydroxide) ions increasing, the silver film may be easily damaged, which affects the sensors durability.

In the proposed sensor, it can be proved that the hydrogel layer can improve the sensing performance of SPR sensors for pH measurement, and also protect the silver film during the measurements. When the pH values increases, a swelling of the hydrogel causes the more absorption of water resulting in the decrease in the RI of the hydrogel because of the hydrogel (n=1.42) has high RI than water (n=1.33). From Fig.5. (b), it can be found that the resonance wavelength experiences blue shift with the pH values increase, and it is consistent with the result of the theory.

In the environment of the acidity and neutral, more carboxyl ions in the hydrogel are dissociated with pH values increase and then result in a swelling of the hydrogel. As shown in Fig.6. (a), with the swelling of hydrogel, its refractive index is reduced, and the resonance wavelength experiences blue shift. Fig.6. (b) shows that the pH sensitivity of the sensor can reach 4.28 nm/pH through linear fitting. The expression of the linear fitting curve is in Eq. (6), where $\lambda_{es}$ is the resonance wavelength, $x_{ac}$ is the pH values range from 1 to 7.

$$\lambda_{es} = -4.28 \cdot x_{ac} + 655.57 \tag{6}$$

As shown in Fig.7. (a), the resonance wavelength experiences red shift with pH value decreased in alkaline condition. The resonance wavelengths for the solutions with the pH range from 8 to 12 as shown in Fig.7. (b). It is found that the resonance wavelength continued to reduce along with pH value increased and to be gentle gradually. It may attribute to the metallic ion concentration is increased with the pH value increased, leading to the increase in the RI of the hydrogel. The maximum sensitivity obtained is about 13 nm/pH in the pH range from 8 to 10. Through the Fig.7. (b) the fitting quadratic curve can be obtained in Eq. (7), where $\lambda_{es}$ is the resonance wavelength, $x_{al}$ is the pH values range from 8 to 12.

$$\lambda_{es} = 1.28 \cdot x^2_{al} - 32.71 \cdot x_{al} + 804.61 \tag{7}$$

In order to confirm the stability of hydrogel-coated optical fiber SPR sensor, we randomly chosen three sensors in our experiments which have been measured after 10 days. All these sensors are fabricated under the same condition strictly. Fig.8 shows the linear fitting results of experimental data. The sensitivities of the three examples are 4.282,4.279 and 4.280 nm/pH in the lower pH region.

The hysteresis characteristic of the sensor was investigated by measuring the resonance wavelength shifts of the sensor in the varying pH in the both ascending and descending processes. In Fig.9, the small fluctuation of the resonance wavelength under the same pH value is measured between ascending and descending processes. The hysteresis percentage of 0.5% can be calculated by using Eq. (8), where $(\Delta Y_H)_{max}$ is maximum fluctuations value of wavelength for ascending and descending processes and $Y_{FS}$ is the difference between the maximum and minimum wavelength. Compared to the previous studies, the sensor has a small hysteresis, which is helpful to increase the accuracy of the pH measurements.

$$Hystersis\% = \left( \frac{(\Delta Y_H)_{\max}}{Y_{FS}} \right) \times 100\% \qquad (8)$$

Fig.10 shows the dynamic responses of the sensor. From Fig.10, the rise time ($t_r$) and the fall time ($t_f$) of the sensor is 24s and 20s, respectively. Because of the measured results had a slight drift, it can demonstrate the dynamic response of the sensor is repeatable. Besides, no significant degradation of sensitivity was observed after several rounds of the experiment.

We also measured the temperature influence of the hydrogel-coated optical fiber SPR sensor response by putting sensing head in sodium hydroxide solution with the temperature raising from 20℃ to 40℃.The transmitted spectra under different temperatures for the hydrogel-coated optical fiber SPR sensor is shown in Fig.11. It may be noted that the resonance wavelength experiences slight blue shift with the temperature increased. Considering that the hydrolysis of the hydrogel is related to temperature, the slight wavelength shift can be explained by the changed of the refractive index of hydrogel. The wavelength shift is about 3 nm towards the shorter wavelength, when the temperature changes from 20℃to 40℃, which gives a temperature sensitivity of -0.15nm/℃. The pH sensitivity of the proposed sensor is 13nm/pH in the pH range from 8 to 10, with one or two orders of magnitude larger than the temperature. Hence, the influence of the temperature fluctuation on the measured results is weak in the range of 20℃ to 40℃.

## 4. Conclusion

In conclusion, a hydrogel-coated optical fiber SPR sensor was proposed. The sensor consisted of a MMF-SMF-MMF structure, and the section of SMF was coated with the sliver film and the hydrogel. The RI of the smart hydrogel will decrease when the pH increases, which cause the resonance wavelength experiences blue shift. The proposed sensor is able to indicate pH variations in a wide range of 1 to 12, and the maximum sensitivity is 13 nm/pH at pH region (8~10 pH). The sensor possesses good stability, prominent sensitivity, remarkable reproducibility and the effect of the temperature could be slight in the range of 20℃ to 40℃. According to the experimental results. The sensor has great potential in the applications of pH measurement, due to the advantage of wide sensing range, high sensitivity and simple fabrication.

## Acknowledgements

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Biography

**Yong Zhao** received the M.A. and Ph.D. degrees, respectively, in precision instrument and automatic measurement with laser and fiber-optic techniques from the Harbin Institute of Technology, Harbin, China, in 1998 and 2001. He was a Postdoctor in the Department of Electronic Engineering of Tsinghua University, from 2001 to 2003, and then was an Associate Professor in the Department of Automation, Tsinghua University of China. In 2006, he was a Visiting Scholar at the University of Illinois in Urbana and Champagne, USA. He is currently a Full Professor with the Northeastern University, Shenyang, China. His current research interests include development of fiber-optic sensors and device, fiber Bragg grating sensors, novel sensor materials and principles, slow light and sensor technology, and optical measurement technologies. He has authored or coauthored more than 190 scientific papers and conference presentations, 8 patents, and 5 books. He is a Member of the Editorial Boards of the international journals such as Sensor Letters, Instrumentation Science and Technology, and the Journal of Sensor Technology.

Figure captions

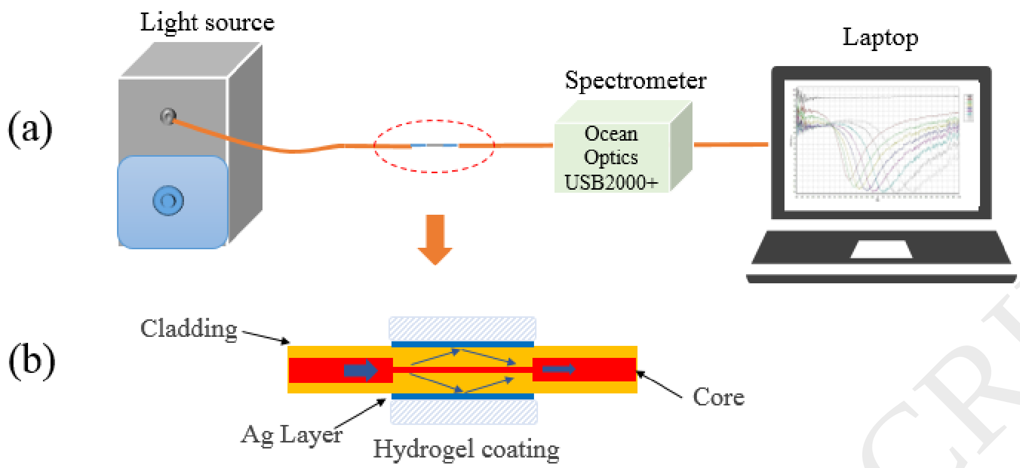



Fig.1. (a) Experimental setup of the sensing system. (b) Schematic of hydrogel-coating optical fiber SPR sensing part

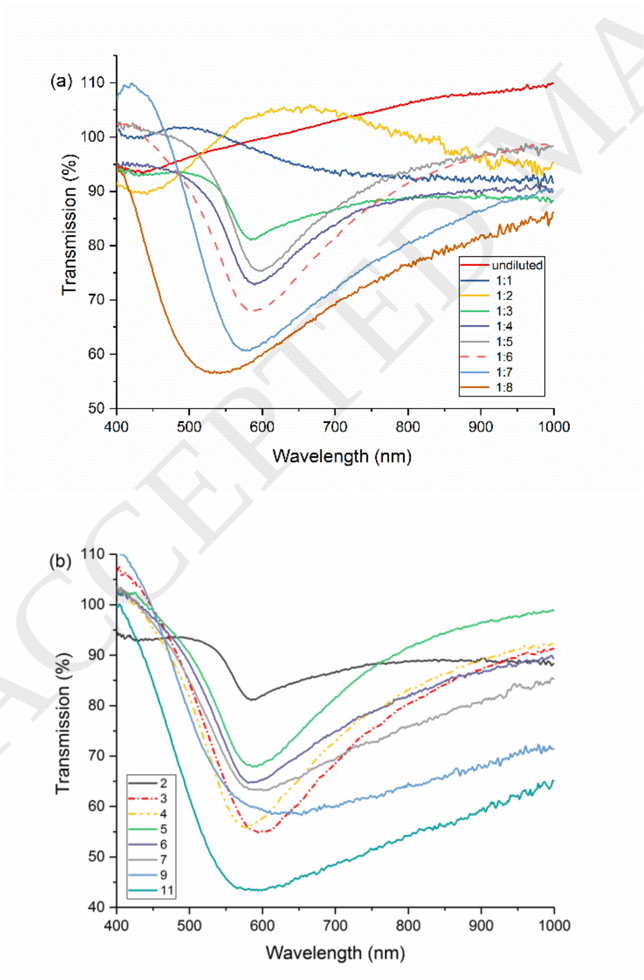
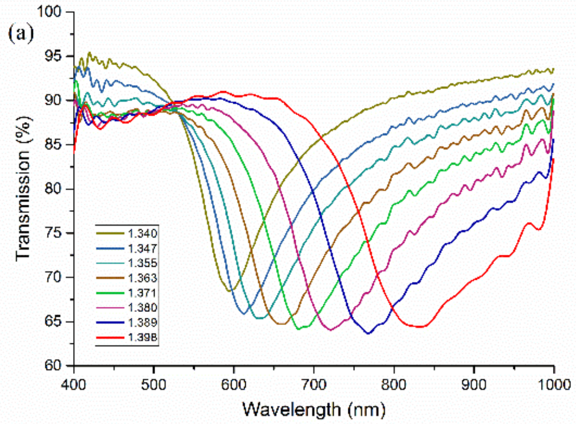


Fig.2 Transmission spectra for the thickness of the mental film with optimum parameter: (a) Transmission spectra at the different diluted rates of Tollen's reagent by fixed five minutes; (b) Transmission spectra at the different deposition time at the fixed the diluted rate of Tollen's reagent.



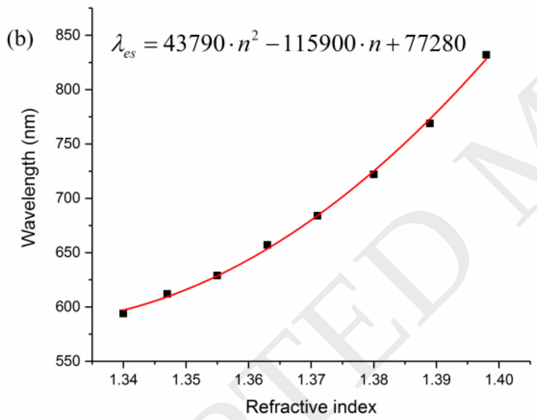




Fig.3 (a) SPR spectra of different refractive index (b) Variation of SPR resonance wavelength of different refractive index

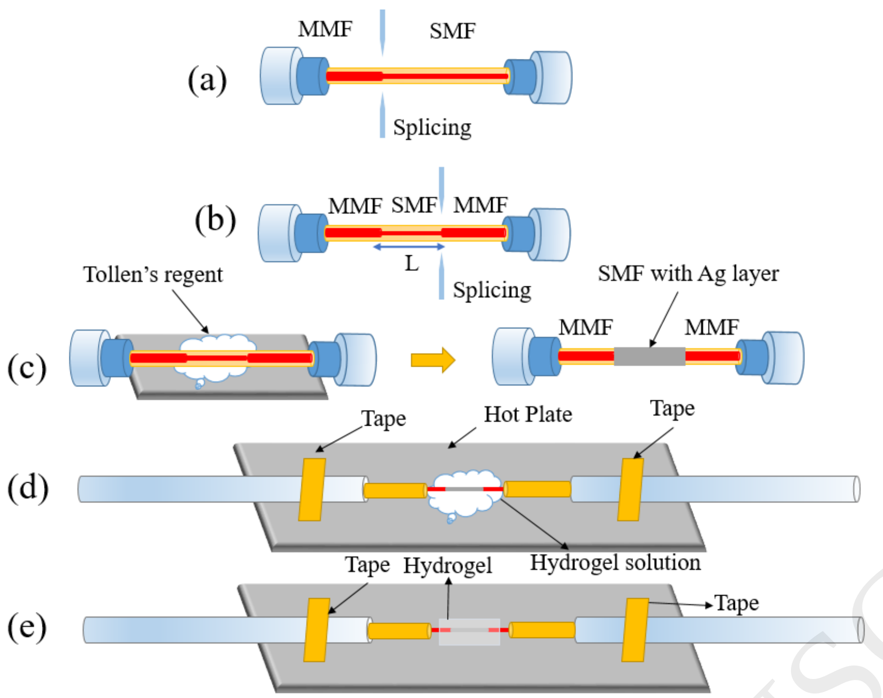
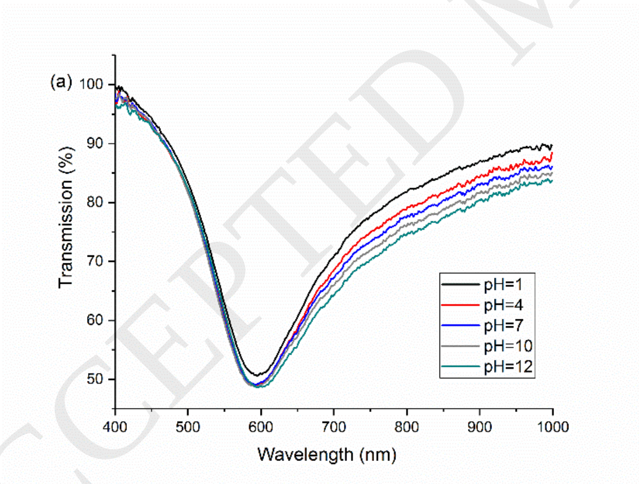



Fig.4 Fabrication process of the sensor: (a)Splicing MMF to SMF, (b)Cleaving to keep only a SMF length of length L then splicing SMF end-face to the same MMF, (c) Coating the SMF with Ag layer, (d) Coating Hydrogel solution on the sensor, (e) Drying the hydrogel



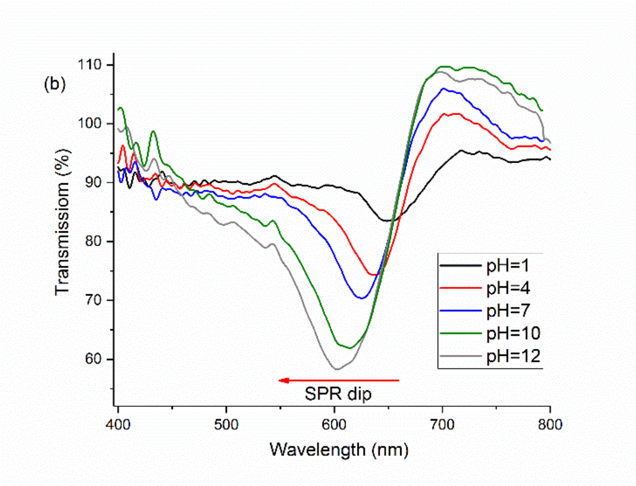



Fig.5. (a) SPR spectra of different pH values without hydrogel. (b) SPR spectra of different pH values with hydrogel

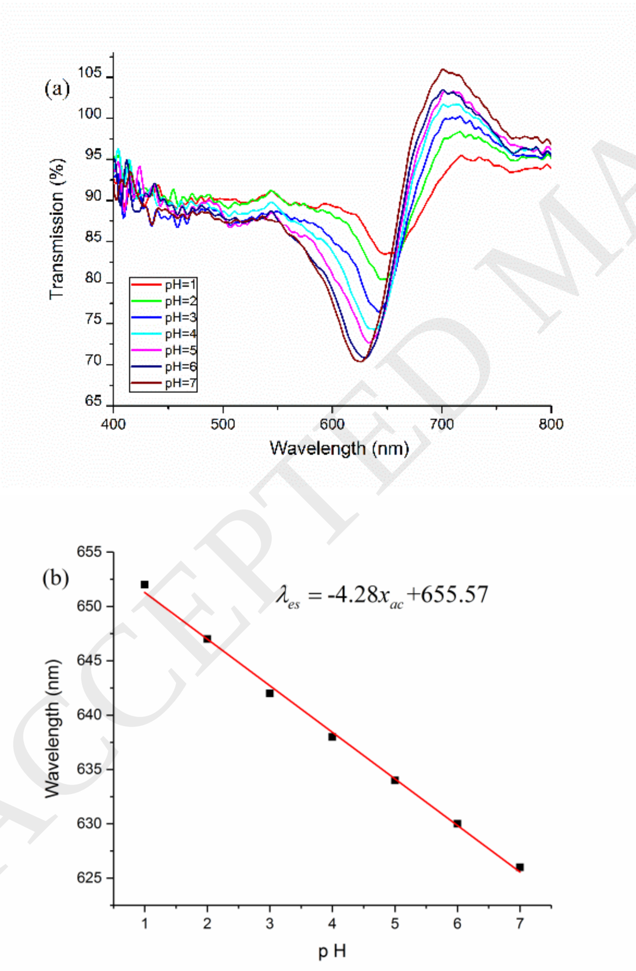



Fig.6. (a) SPR spectra of pH range from 1 to 7 at 22℃. (b) Variation of SPR resonance wavelength of pH range from 1 to 7 at 22℃

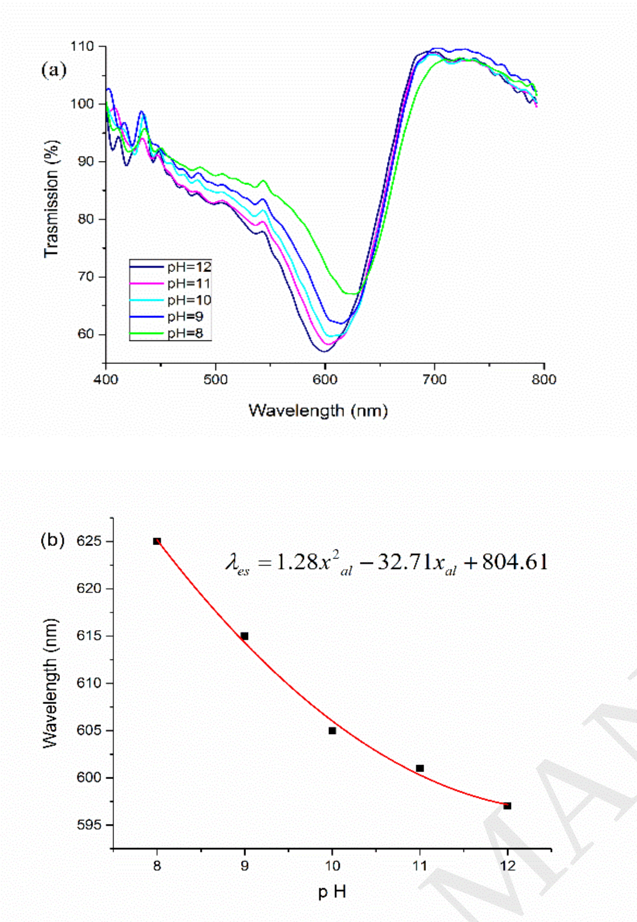



Fig.7 (a) SPR spectra of pH range from 8 to 12 at 22℃. (b) Variation of SPR resonance wavelength of pH range from 8 to 12 at 22℃.

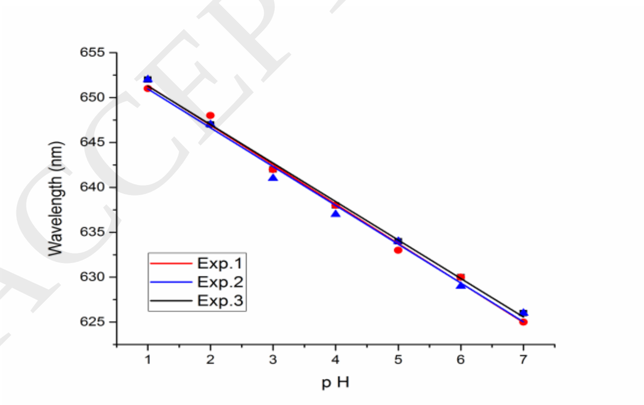



Fig.8 Three examples of pH wavelength curve which are chosen randomly in 10 experimental data.

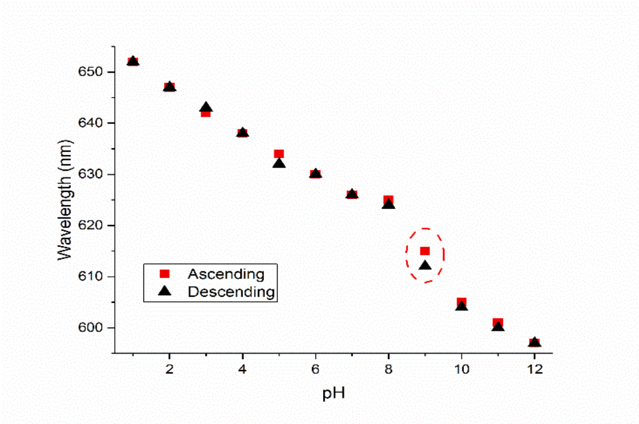



Fig.9 Wavelength shift of the proposed pH sensor versus pH values in both ascending and descending orders.

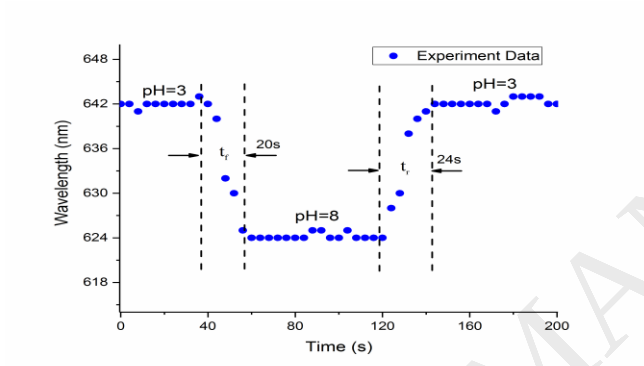



Fig.10 Reproducibility of the proposed pH sensor between pH 3 and 8.

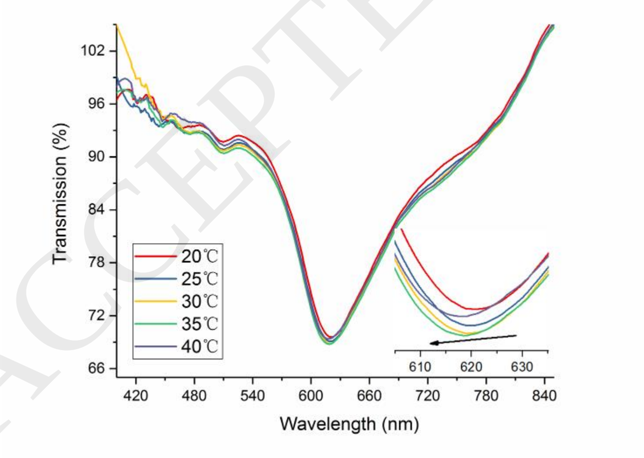



Fig.11 SPR spectra of temperature range from 20℃ to 40℃ at pH=8