Research Article | Vol. 26, No. 11 | 28 May 2018 | OPTICS EXPRESS 14610
Optics EXPRESS

All-polymer fiber-optic pH sensor

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Abstract: A novel all-polymer fiber-optic pH sensor using a UV-cured pH-sensitive hydrogel, poly(ethylene glycol) diacrylate (PEGDA), coated on a polymer fiber Bragg grating was developed. The PEGDA increased in volume according to the pH value of the surrounding fluid, which subsequently induced a lateral stress in the polymer fiber Bragg grating. The proposed pH sensor exhibits a pH sensitivity of up to –0.41 nm/pH and a fast response time of 30 s.

OCIS codes: (060.2370) Fiber optics sensors; (060.3735) Fiber Bragg gratings; (160.5470) Polymers.

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#328285 https://doi.org/10.1364/OE.26.014610
Journal © 2018 Received 16 Apr 2018; revised 12 May 2018; accepted 14 May 2018; published 23 May 2018

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1. Introduction

pH measurement is crucial for many industries, such as, biological, ecological, environmental science, clinical medicine, and civil engineering. For example, in wood production, pH is a recognized indicator used to examine the wood condition, providing essential information about the bacterial pollution and healing stage [1]. In recent years, substantial efforts were invested towards improving the performance of pH sensors while reducing their cost. Fiber-optic pH sensors have been proposed due to their numerous advantages, including small size, immunity to electromagnetic interferences, potential low-cost, and multiplexed detection capability. Several types of fiber-optic sensors have been reported in research articles. A type of fiber-optic pH sensors is based on the pH indicator being immobilized in matrix materials. The reported pH indicators include both single organic molecules [2,3] and mixture components [4]. Optical properties, such as, absorbance [1,5,6] and fluorescence [4,7,8], can be utilized to determine the pH of tested solutions. Another type of pH sensors–based on fiber-optics–employed sol-gel technology to fabricate microstructures on optical fibers. The amount of swelling of the microstructures is influenced by the pH value, which subsequently induces a change in the sol-gel's refractive index [9–12]. Absorption- or fluorescence-based pH sensors have some inherent disadvantages, because they are easily affected by light intensity fluctuations, temperature, and the concentration of indicators, and, therefore, are not reliable [10].

In order to achieve reliable and accurate pH measurements, several pH sensing schemes have been demonstrated based on titled fiber Bragg grating (TFBG), resonant optical responses and modal interferometers. A. Lopez Aldaba *et al.* recently presented pH sensing based on TFBG coated with Polyaniline [13]. Y.Z. Zheng *et al.* demonstrated a pH fiber

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sensor using a Fabry–Perot interferometer with polyvinyl alcohol (PVA)/poly-acrylic acid (PAA) hydrogel coated on a fiber end-face [12]. Corres *et al*. reported a pH sensor using a long-period grating (LPG) coated with PAA and poly(allylamine hydrochloride)(PAH) [11]. Gu *et al.* demonstrated a pH sensor based on a fiber interferometer constructed with a thin core fiber coated with PAA and PAH, and fusion spliced to single mode fibers on both ends [10,13–15]. Zhao *et al.* also reported a pH sensor with high sensitivity and a fast response time of 5 s based on a modal interferometer fabricated from thin-core fibers coated with poly(ionic liquid)s and PAA [16]. Every aforementioned optical method is based on silica fibers, which are fragile and produce shards upon brakeage. Thus, they are not suitable for in vivo tests or as wearable sensors.

Polymer optical fibers (POF) based on poly(methyl methacrylate) (PMMA) offer more flexibility, do not break easily, recycling use in LCD monitors and exhibit good biocompatibility [17–21] compared with silica fibers. Rovati *et al.* reported a pH sensor consisting of a PMMA fiber coated with a sol-gel to detect the absorbance of phenol red under various pH solutions [6]. Zamarreño, C. R. *et al.* demonstrated a pH sensor based on a micro structured POF by detecting dye-doped fluorescence intensity [22]. However, these methods are not stable since the absorbance can be easily affected by changes in light intensity, temperature, and concentration of indicators.

In this paper, we demonstrate a novel all-polymer pH sensor consisting of a UV-cured poly(ethylene glycol) diacrylate (PEGDA) coating on a single-mode polymer optical fiber inscribed with a Bragg grating. PEGDA is a pH-sensitive hydrogel and is easy to be fabricated (e.g. simply curried under UV lamp). Furthermore, it is good choice to be used in biomedical application due to its bio-compatibility [23,24]. This novel polymer fiber-optic sensor exhibits a sensitivity of up to −0.41 nm/pH and an average response time of 30 s. As the sensor was developed toward bio-medical application, only acidic range was considered [24].

2. Fabrication of the pH sensor

The photosensitive single-mode polymer optical fibers (POFs) used in the experiment were fabricated in-house. The polymer preforms were prepared using the "pull-through" technique described in [25]. A cladding preform, made of pure PMMA, with an outer diameter of 19.6 mm and a 0.95 mm diameter hollow hole in the center was fabricated. A 13 mm diameter core preform, consisting of 5% benzyl methacrylate and 1 wt.% benzyl dimethyl ketal (BDK)–which is photosensitive to UV light and can produce a higher refractive index modulation after UV irradiation–was also manufactured, permitting to shorten the sensor fabrication time [26]. All the preforms were fabricated in a glove box. The POF preform–with the core preform inserted inside the cladding preform–was drawn into fiber with an in-house fiber drawing tower. The diameter of the photosensitive POF and its core were 125 and 6.5 μm, respectively. The diameter of the fabricated POF is the same as that of commercial standard single-mode silica optical fibers to simplify the connection of the POF to standard single-mode fibers.

A fiber Bragg grating (FBG) was inscribed in the POF using the phase mask technology with a 325 nm-He-Cd laser (KIMMON IR3501R-G). Bragg gratings can be inscribed in the photosensitive POF in about 30 s with the laser output power set to 48 mW.

Figure 1(a) shows the 1 mm × 1 mm square cross-section of the pH sensor, in which the single-mode POF is encapsulated at the center of the UV-cured PEGDA. Figure 1(b) shows the mold used to fabricate the pH sensor. The mold consists of a groove–1 mm wide, 1 mm deep, and about 15 mm long–and was made from microscope glass slides. Top view of the UV-cured pH sensor is shown in the inset of Fig. 1(b). The PEGDA solution was cured in 2 min using a 365 nm UV lamp (PM100D, S120VC, Thorlabs) with a power density of about 27 mW/cm^2.

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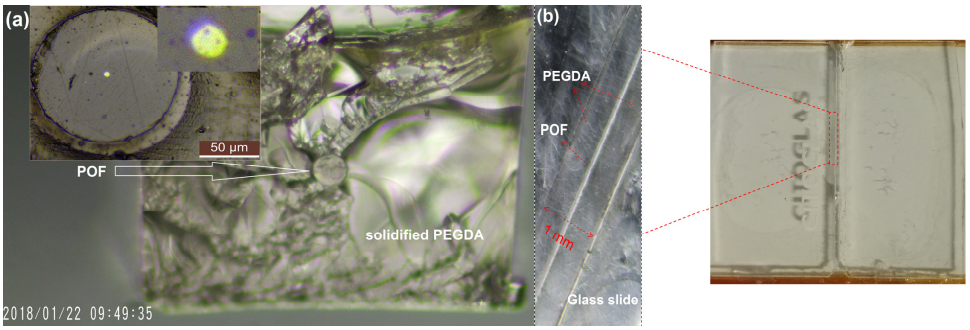

Fig. 1. (a) Cross section of the pH sensor showing the POF encapsulated in the center of the UV-cured PEGDA. Inset: the cross section of core area of POF: the length of max and minor axes are 5.7μm and 5.0μm, respectively (b) Top view of the mold with a 1 mm wide and 1 mm deep groove for fabricating the pH sensor. The inset shows the fabricated sensor.

3. Results and discussion

The POFBG pH sensor was evaluated by immersing it in aqueous solutions of hydrochloric acid with pH values between 0 and 6.5. Figure 2(a) shows the spectral response of the POFBG pH sensor, which was recorded using interrogator from MOI (SM125) with 1pm wavelength resolution. We can see that the single-mode FBG spectrum has two peaks. This is because the fiber core is slightly elliptical; therefore, the POF possesses birefringence and the two reflection peaks correspond to the two orthogonal polarizations of the fiber. The peak wavelength shifts to a longer wavelength when the pH decreases from 6.5 to 3. This is due to the higher hydrogen ion concentration in the hydrochloric acid solution with a smaller pH value, allowing more hydrogen ions to combine with the oxygen atoms in the PEGDA. Therefore, the hydrophilic property of the solidified PEGDA is significantly improved. As a result, the amount of swelling of the solidified PEGDA increases, and thus, more pressure is exerted on the POFBG.

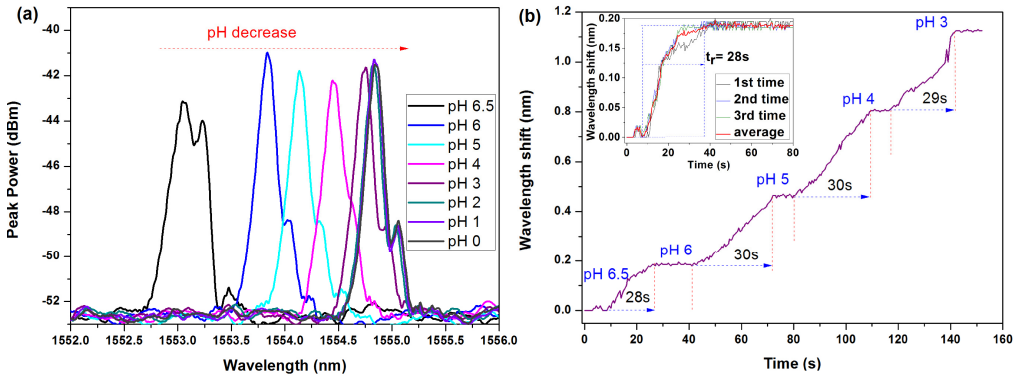

Fig. 2. Wavelength response of the sensor to solutions of different pH values: (a) spectrum shift as function of pH (b) response time(t_r) with different pH values—inset: the average response time in the pH range of 6.5–6.

We investigated the response time of the POFBG pH sensors in solutions with pH values varying from 6.5 to 3. The results in Fig. 2(b) show that the average response time is about 30 s. The inset in Fig. 2(b) shows the results of 3 experiments with pH values varying from 6.5 to 6.0, with an average response time of 28 s. The results clearly show that the reflection peak wavelength increases with smaller pH values. Every unit change of the pH has a response time of about 30 s, similar to the average time calculated using the method reported by Dr. Gu *et al.* [10]. The sensitivity of the POFBG pH sensor made with a 125 μm thick POF is −0.34 nm/pH in the pH range of 3–6.5. However, as the pH decreases further, the wavelength of the

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sensor changes only slightly. This is related to the saturation phenomenon originating from the full protonation of the solidified PEGDA, which prevents it from further swelling [27].

The sensitivity of the PEGDA pH sensor with respect to POF diameters was also investigated. POFs with a diameter of 125 µm were etched down to 92 µm and 105 µm using the etching method reported by Dr. Hu *et al*. [28]. FBGs were inscribed in the POFs with diameters of 92 µm, 105 µm, and 125 µm. The wavelength shifts of the three POFBGs coated with PEGDA, immersed in solutions with pH values of 0–6.5 were measured and are shown in Fig. 3. The results show that a higher sensitivity is obtained with thinner POFs. The sensitivity of the 92 µm thick POFBG is about 20% higher than the 125 µm thick one. This is expected as thinner POFs have less cladding material between the FBG in the fiber core and the PEGDA. POFs thinner than 92 µm were not investigated due to their excessive softness, rendering them inappropriate for handling, and hence, difficult to obtain a uniform solidified PEGDA coating on them.

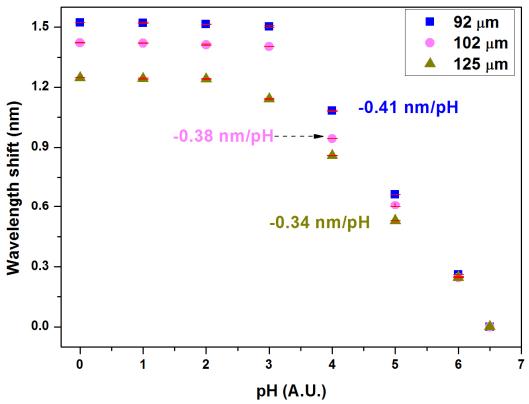

Fig. 3. Different diameter POFBG coated with PEGDA immerged in solutions of different pH values.

Figure 4 shows the measurement of the POFBGs with and without the PEGDA coating. The results clearly show that POFBG without PEGDA coating is not sensitive to pH.

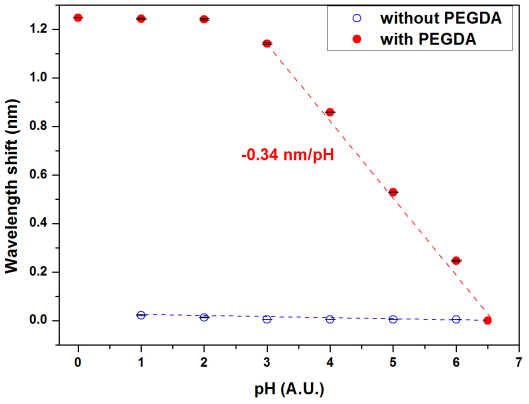

Fig. 4. pH measurement using POFs with and without PEGDA coating.

The sensitivity and response time of the PEGDA pH sensor with respect to the solidified PEGDA of different thicknesses were also investigated. FBGs were inscribed in three 125 µm thick POFs which were subsequently coated with different thicknesses of solidified PEGDA with their cross-sectional dimensions being 1 mm × 1 mm, 0.75 mm × 0.75 mm, and 0.5 mm × 0.5 mm. The pH sensitivity and response time of these three sensors were measured in aqueous solutions of hydrochloric acid with pH values of 0–6.5. All three sensors exhibited a

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linear response to pH values of 3.0–6.5. As expected, the sensor with the thickest solidified PEGDA has the highest sensitivity but the slowest response time, as shown in Fig. 5(a) and Fig. 5(b), respectively. Indeed the thicker solidified PEGDA, the stronger will be the strain applied to the fiber. Furthermore, the response time is inversely proportional to the material thickness as it is related to diffusion process.

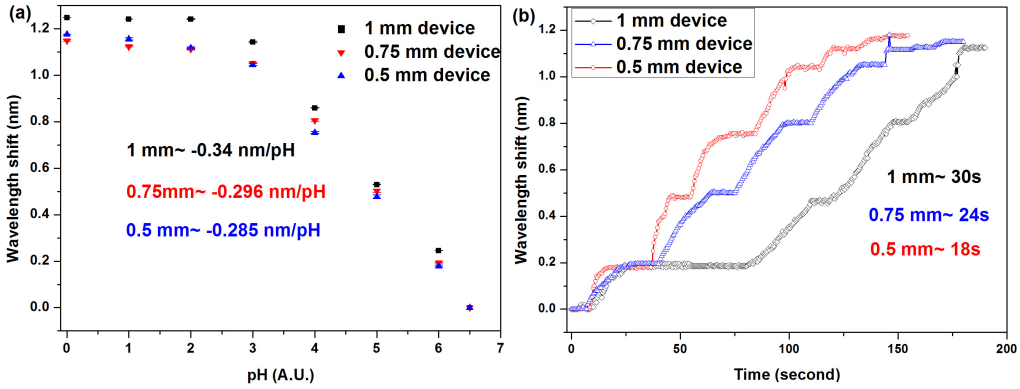

Fig. 5. PEGDA POFBG sensors with varying thickness: (a) response sensitivity, and (b) step response time.

The influence of the temperature on the wavelength shift of the PEGDA pH sensor was also evaluated by placing the sensor in an environmental chamber set at 50% relative humidity, and cycling the temperature between 20 °C and 45 °C with 5 °C steps. The results of three temperature cycles are shown in Fig. 6(a). The results exhibited high reproducibility. In addition, Fig. 6(b) shows that the sensor exhibits a linear response with a temperature sensitivity of 10 pm/°C, similar to that of fused silica glass fibers [29].

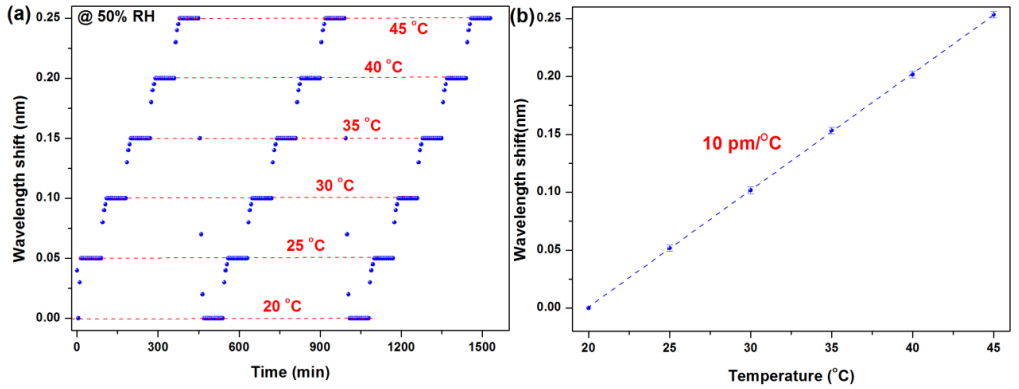

Fig. 6. Temperature response of the POFBG pH sensor.

Typically, POFBGs exhibit a blue shift with changing temperature with a coefficient of –45 to –70 pm/°C [30,31]. However, the POFBG coated with PEGDA exhibits a red shift with changing temperature with a coefficient of + 10 pm/°C. This is because the solidified PEGDA exhibits a relatively large thermal expansion coefficient of approximately 1.56×10^{-4} K^{-1} [32].Table 1 compares the performance of the proposed polymer optical-fiber based pH sensor with that of pH sensors made from fused silica glass optical fibers. And the comparison only focuses on the acidic range to match the purpose of this presented work. As far as the authors are aware, no other pH sensors based on POF have been reported.

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Table 1. Sensor Performance of the Present System Compared to Other pH Fiber-optics Sensors based on Glass Fibers in acidic range

Polymer coating	Fiber type	Ease of fabrication	Sensitivity	Work range	Responsive time	Reference
$(PAH/PAA)_{25}$	LPG based on SMF	Medium	28.3 nm/pH	pH 4~7	T_r = 120 s; T_f = 270 s	11
PVA/PAA	Hollow-core PCF sandwiched between SMFs	Complex	11 nm/pH	pH 4.3~6.9	–	12
PEGDA	POF	Simple	–0.34 nm/pH	pH 2~6.5	T_r = 30 s	Present work

4. Conclusion

A novel type of fiber-optic pH sensor based on a FBG inscribed in a polymer optical fiber was presented. It was demonstrated that PEGDA produces different degrees of swelling when immersed in aqueous solutions of hydrochloric acid with varying pH values. This phenomenon is exploited to exert lateral stress to induce a wavelength shift in the POFBG. We demonstrated a high sensitivity of –0.34 nm/pH. In addition, a fast response time of 30 s can be achieved with the proposed pH sensor. The main advantages of the proposed pH sensor are its ease of handling, and applicability in vivo or for medical applications.

Funding

National Natural Science Foundation of China (NSFC) (1701268); Hong Kong Research Grant Council's General Research Fund Project (152207/15E); Hong Kong Polytechnic University (1-ZVGB).