Optical Fiber Technology 20 (2014) 28–31

Contents lists available at ScienceDirect

Optical Fiber Technology

www.elsevier.com/locate/yofte

A fiber-optic pH sensor based on relative Fresnel reflection technique and biocompatible coating

Jiao-Yang Li [a,b], Xu-Guang Huang [a,*], Wei Xu [a], Dong-Rui Xiao [a], Ze-Bing Zhong [a]

[a] Laboratory of Nanophotonic Functional Materials and Devices, School of Information and Optoelectric Science and Engineering, South China Normal University, Guangzhou 510006, China
[b] School of Physics and Engineering, Sun Yat-sen University, Guangzhou 510275, China

ARTICLE INFO

Article history:
Received 22 April 2013
Revised 7 October 2013
Available online 2 December 2013

Keywords:
Electrostatic self-assembly
Relative Fresnel reflection technique
Biocompatible coating
PH biosensors

ABSTRACT

A biocompatible fiber-optic pH sensor based on Fresnel reflection technique and a sensing coating is presented. Sodium alginate and polyethylenimine are alternatively deposited on the sensing fiber end to form the sensing coating via a layer-by-layer electrostatic self-assembly technique. An optical switch is added to the measurement system for the convenience of fast calibration. A linear, monotonic and fast response in a large pH range (from pH 5.87 to pH 10.55) is obtained with the resolution of 0.01 pH unit. The sensitivity of the pH sensor is 0.018 R.I.U/pH. It is not influenced by fluctuations of light source.

1. Introduction

The measurement and monitoring of pH is important in chemical, biomedical and environmental sciences for applications such as water quality test, food production process, blood test, oil gas monitor, etc. The conventional and commercial pH sensors are based on pH sensitive glass membrane electrode utilizing potentiometric technique. They have relatively short response time, good accuracy and repeatability, but they are difficult to be miniaturized and not suitable for biosensing because of electrical connection. In the last decade, optical pH sensors have attracted much interest and technical efforts because of its various advantages over conventional potentiometric based pH sensors such as small size, immunity to electromagnetic interference, remote sensing capability and suitable for biocompatible applications.

Various kinds of fiber-optic pH sensing techniques have been proposed and demonstrated. The pH indicators immobilized in sensing films were used to monitor pH values of aqueous solutions by utilizing the indicators' properties such as absorbance and fluorescence intensity [1–4]. The indicators usually are organic dyes which have inherent drawbacks that the dyes are likely to be bleaching and leaching from host materials. Smart coatings onto an optical fiber prepared by chemical oxidation [3] or sol–gel dip-coating technology [4,5] were proposed to be sensing elements, as the properties of the coatings such as refractive index, surface area, thickness and absorbance have relationship with pH value [6].

Micro and nano-structured fiber sensors have attracted the attention of researchers because of their advantages of high sensitivity, small sensor head and academic interest [6,7]. One type of ultrathin coating based fiber-optic pH sensor is utilizing pH-dependence morphology change of the weak polyelectrolyte chains, usually known as swelling/deswelling. The sensing coatings are usually prepared by using electrostatic self-assembly (ESA) deposition technique, which has lots of advantages over other methods in preparing multilayer thin film: independency of the size and shape of the substrate, the thickness of coating is controlled with nanoscale precision, ease of fabrication, etc. The adsorption is mainly occurred between polycations and polyanions by electrostatic interactions. The swelling/deswelling of the nanocoating results in the change in its refractive index. Therefore the sensor can be designed for refractive index measurement, and various optical designs have been proposed such as nanocoatings deposited onto the surface of an LPG [8], a tapered single-mode fiber [9], a thin-core fiber modal interferometer [10,11], or to form a Fabry-Perot nanocavity [12].The polyelectrolytes used in the building-up of the self-assembled coating usually are poly(allylamine hydrochloride) (PAH) as polycation and poly(acrylic acid) (PAA) as polyanion. However, the PAA/PAH coating based pH sensors have opposite monotonicity at acid and alkaline solutions, which is not convenient in actual measurements.

In this paper, we proposed a new type of fiber-optic pH sensor based on the pH-change-induced swelling/deswelling of a sensing coating which was deposited on a fiber end using electrostatic self-assembly technique. Polyethylenimine (PEI) was used as polycation, while sodium alginate (SA) was used as polyanion. A

* Corresponding author.
E-mail address: huangxg@scnu.edu.cn (X.-G. Huang).

1068-5200/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.yofte.2013.11.002

relative Fresnel reflection technique was used to measure the refractive index of the sensing coating, as the change in refractive index caused a change in the Fresnel reflective intensity. The resolution of the refractive index (RI) interrogation scheme is 10^{-4} RI unit, which is precise for us to develop a pH-change-induced RI measurement system. Experimental results show that the refractive index decreases with an increase in pH value of the aqueous solutions. Furthermore, the sensor possesses a monotonic response in a large pH range, stability and high sensitivity.

2. Theoretical considerations

Sodium alginate (SA), which is obtained from marine brown algae, is widely used in food and pharmaceutical industries. It is dissolvable in water because of the hydrophilic nature. Since the hydrophilicity of the polymer depends on pH values, the polymer is of swelling/deswelling behavior in different pH solutions [13]. SA is easy to be fabricated into films. Furthermore, it has some unique properties such as non-toxicity, biocompatibility, biodegradability, hydrophilicity and relatively low cost. Polyethylenimine (PEI) is a cationic polyelectrolyte with high cationic density and good performance in adhesion and adsorption. Therefore, one can use SA and PEI to form a biocompatible sensing film. The swelling/deswelling of the PEI/SA coating will result in the change in its refractive index. The two biocompatible polymers are alternatively self-assembled on the end surface of the single mode fiber to form a fiber-optic pH biosensor.

The ESA method is shown schematically in Fig. 1. First, the fiber end was immersed into piranha solution (H_2SO_4 and H_2O_2 in the concentration of 7:3), which was headed to be boiling for about 10 min. Then it was washed with large amount of deionized water and dried with nitrogen gas. The fiber end, which was negatively charged after these treatments, was then immersed into PEI and SA alternatively with the reaction of 10 min to form a monolayer of polymer through electrostatic adsorption. After each monolayer was formed, the fiber was rinsed with deionized water for 1 min to remove the excess molecules. Each polycation/polyanion layer (PEI/SA) is called a bilayer. After depositing 10 bilayers, the optical fiber end was baked in an oven at 60 °C for 10 h.

The experiment setup of the proposed system is shown in Fig. 2. It consists of a broad band source (BBS) operating in the wavelength around 1550 nm, three single-mode fused couplers, an optical switch, two photodetectors (PDs) and three optical fibers with sensing ends. Splitting ratios of Coupler 1, 2 and 3 are all 50:50. The fiber sensing ends, which are placed into standard telecommunication ferrules with a diameter of 2.5 mm for protection and ease of cleaning, are vertically planar surfaces. All the fibers are Corning SMF-28 fibers. The light emitted from the BBS is equally split into two beams (Beam 1 and Beam 2, shown in Fig. 2) by Coupler 3. The light of beam 1 through Coupler 1 and the optical switch in sequence is finally reflected on the fiber-film interface (in channel 1), or on the fiber-air interface (in channel 2), while the light of beam 2 (as a reference beam) through Coupler 2 is reflected on the fiber-air interface. Two bend-loss-based fiber attenuators with −50 dB attenuation are implemented to remove the unwanted reflections. Two reflected light from sensing end and reference beam are detected by PD 1 and PD2, respectively. In order to eliminate the time-varying instability of the detection system, we calibrated this system every ten minutes. During the calibration, the output channel of the optical switch was switched to channel 2, therefore the intensities received by PD 1 and PD 2 were both the reflective intensity from the fiber-air interface.

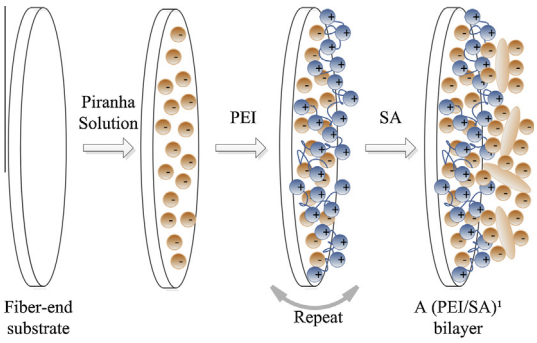

Fig. 1. Schematic of ESA deposition process.

As the BBS is an incoherent source, there is no interference, if any backreflections enters the source. The return loss of the couplers in the system is −60 dB, and all of the fiber ends of the couplers and the optical switch were fused to achieve very low backreflections. Therefore, the influence of backreflections on the optical source should be very little, even without an isolator inserted right after the source. In addition, the multichannel measurement system can effectively eliminate the fluctuation of the light source, propagation losses and the influence of the environment.

Assuming that I_0 is the output intensity of the light source, n_f, n_{air} and n_{coat} are the refractive indices of the fiber, air and SA/PEI coating, respectively. The k_1, k_1', k_2, k_2', k_3, k_3' are the transmittances of the bar state or cross state of Couplers 1, 2, 3, respectively. The k_4, k_4' are the transmittances of channel 1 and channel 2 of the optical switch. The η_1, η_2 are the quantum efficiencies of PD 1 and PD 2. When channel 1 of the optical switch is open, the intensity I_1 received by PD 1 can be calculated by the Fresnel formula [14]:

$$I_1(t) = \eta_1(t)(k_4)^2 k_1 k_1' k_3 I_0 \left(\frac{n_f - n_{coat}}{n_f + n_{coat}}\right)^2. \quad (1)$$

When channel 2 of the optical switch is open, the intensity I_2 received by PD 1 can be calculated by

$$I_2(t) = \eta_1(t)(k_4')^2 k_1 k_1' k_3 I_0 \left(\frac{n_f - n_{air}}{n_f + n_{air}}\right)^2. \quad (2)$$

Likewise, the intensity I_3 detected by PD 2 is given by

$$I_3(t) = \eta_2(t) k_2 k_2' k_3' I_0 \left(\frac{n_f - n_{air}}{n_f + n_{air}}\right)^2. \quad (3)$$

From Eqs. (2) and (3), one can obtain the relative reflective intensity R_{air} as follows:

$$R_{air}(t) = \frac{I_2(t)}{I_3(t)} = \frac{\eta_1(t)}{\eta_2(t)} K (k_4')^2. \quad (4)$$

And from Eqs. (1) and (3), one can obtain the relative reflective intensity R as follows:

$$R(t) = \frac{I_1(t)}{I_3(t)} = \frac{\eta_1(t)}{\eta_2(t)} K (k_4)^2 \left(\frac{R_1}{R_2}\right)^2, \quad (5)$$

where $K = (k_1 k_1' k_3)/(k_2 k_2' k_3')$, $R_1 = \left(\frac{n_f - n_{coat}}{n_f + n_{coat}}\right)^2$ and $R_2 = \left(\frac{n_f - n_{air}}{n_f + n_{air}}\right)^2$.

At the time $t = t_0$, channel 2 of the optical switch is turned on, so one can get the relative reflective intensity R_{air}:

$$R_{air}(t_0) = \frac{I_2(t_0)}{I_3(t_0)} = \frac{\eta_1(t_0)}{\eta_2(t_0)} K (k_4')^2. \quad (6)$$

After that, we turn on channel 1 of the optical switch immediately. The relative reflective intensity R can be expressed as: