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Non-enzymatic glucose detection based on phenylboronic acid modified optical fibers

Xiaolan Sun [a,*], Nana Li [a], Bin Zhou [a], Wei Zhao [a], Liyuan Liu [a], Chao Huang [a], Longfei Ma [b], Alan R. Kost [c]

[a] Key Laboratory of Specialty Fiber Optics and Optical Access Networks, Joint International Research Laboratory of Specialty Fiber Optics and Advanced Communication, Shanghai Institute for Advanced Communication and Data Science, School of Communication and Information Engineering, Shanghai University, Shanghai 200444, China

[b] Ruijinerlu Community Health Service Center of Huangpu District, Shanghai 200025, China

[c] College of Optical Sciences, The University of Arizona, Tucson, AZ 85721-0094, USA

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ABSTRACT

A non-enzymatic, sensitive glucose sensor was fabricated based on an evanescent wave absorbing optical fiber probe. The optical fiber sensor was functionalized by fixing a poly (phenylboronic acid) (polyPBA) film onto the conical region of the single mode fiber. The reflected light intensity of the polyPBA-functionalized fiber sensor increased proportionally with glucose concentration in the range of 0–60 mM, and the sensor showed good reproducibility and stability. The developed sensor possessed a high sensitivity of 0.1787%/mM and good linearity. The measurement of glucose concentration in human serum was also demonstrated.

1. Introduction

Optical fiber biosensors [1] have been extensively applied in the fields of protein recognition [2], cell measurement [3] and genetic detection [4] on account of their high accuracy, high efficiency, low cost, operational convenience and good biological compatibility. There are several different types of fiber biosensors, including those based on U-bent fibers [5], different-angle tilted gratings [6], long period gratings [7], D-shaped optical fibers [8], and spliced special fibers [9]. Although these sensory structures have gained popularity, they suffer weaknesses including complex fabrication processes and low sensitivity. In recent years, sensors based on tapered fibers have attracted much attention in biosensing. Tapered fibers have the advantage of coupling evanescent waves between core modes and cladding modes, which enhances the sensing parameters of sensors. For instance, tapered single mode and multimode fibers used for both strain and temperature sensing have demonstrated resolutions of ±1.6 °C and ±5.6 $\mu\varepsilon$, respectively, continuous monitoring of the salinity of sodium chloride solution with a sensitivity of 0.0024 mV/%, and protein detection with a sensitivity of 2.42141 nm/%W/V [10–12]. However, the abovementioned sensors utilized biconically tapered optical fiber in the sensing section and transmission spectra as the sensing signal. Despite the fact that the transmission spectra are stable and that the high transmitted power leads to high sensitivity, when it comes to some special sensing applications such as living body monitoring, fiber sensors with terminal reflection structure are preferable [13,14]. Terminal reflection fiber sensors have the unique property of minimal invasion [15,16].

Diabetes has become a worldwide health challenge so that numerous efforts have been dedicated to glucose sensing [17–19]. Fluorescently labeled sensing schemes employ changes in fluorescent intensity to reflect sample concentration and have become one of the key methods for glucose sensing [20]. However, the short lifetime of fluorescent agents and the high cost of enzymes limit their further development and application in biosensing [21]. Therefore, developing more robust and low-cost sensing methods is highly desirable to promote their widespread use in clinical settings.

Phenylboronic acid (PBA) can rapidly form high-affinity, reversible covalent bonds with glucose to generate boronate esters in basic aqueous media, and has been extensively exploited as a glucose receptor [22–24]. For example, PBA has been applied to electrochemical amplification for glucose detection based on the PBA-glucose interaction, coupled with a redox cycling and nanomaterials amplification effect [25,26]. In addition, polymers with PBA units have been previously used for glucose sensing and insulin delivery through modulation of electrostatics upon glucose binding to PBA [27,28]. Nevertheless, fabrication for these sensory schemes, including fabrication on graphene or carbon nanotubes, require complex procedures and high cost.

* Corresponding author.
E-mail address: xiaolansun@shu.edu.cn (X. Sun).

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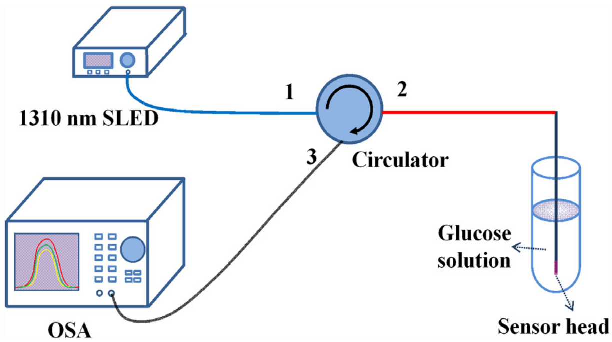

Fig. 1. Schematic diagram of tapered SMF optical fiber sensor.

In this paper, we propose a simple tapered SMF glucose sensor, based on the reversible complexation of glucose with a polyPBA film grown on the cone area of a fiber probe. By measuring the reflected light intensity of the glucose biosensor, the optical fiber system can be used to test glucose concentration in human serum samples without resorting to the use of glucose oxidase. The PBA modified optical fiber sensor is highly sensitive, reversible, and stable.

2. Materials and methods

2.1. Fabrication of the tapered fiber probe

A standard SMF with core and cladding diameter of 8.5 um and 125 um, respectively, was used in this study. The fabrication of this tapered fiber was carried out with a fusion splicer. First, approximately 2 cm of the protective coating of the fiber was removed using a fiber stripper, and then the fiber was cleaned with alcohol. Next, the coating-removed fiber was put into a fusion splicer to obtain a prematurely tapered fiber. Then, the tapered fiber, covered by a layer of isooctane, was put into hydrofluoric acid (HF) for about 8 min to form a tapered tip with a better symmetry.

2.2. Surface modification for the sensor tip

Prior to the deposition of the polyPBA film, the region of the optical fiber probe that was made as described in Section 2.1, was soaked in distilled water for 10 min and then immersed into a 1 wt% ethanolic KOH solution for 20 min to form hydroxyl groups. The fiber tip was then immersed into a 2% solution of 3-aminopropyltrimethoxysilane (APTMS) in dry toluene for 30 min. Subsequently, the fiber tip was immersed into a N,N-dimethylformamide (DMF) solution containing 1 wt% PBA and 2.3 wt% 2,2-azobisisobutyronitrile (AIBN) in a nitrogen atmosphere for 3 h at 70 °C to finish the polyPBA coating. Finally, the tip was washed with DMF.

2.3. Experimental setup

The tapered SMF optical fiber sensor, schematically depicted in Fig. 1, is composed of a light source, an optical spectrum analyzer (OSA, Yokogawa, AQ6370B), a circulator, and a reaction zone. We used a super luminescence light emitted diode (SLED) to generate 1310 nm-wavelength light that is introduced into the first port of an optical circulator. For reflectance spectra measurement, the second port of the circulator was connected to the reaction tip, and the signal reflected from the fiber probe was collected by the OSA, which was connected to the third port of the circulator. The spectra were analyzed using Origin graphing and analysis software.

3. Results and discussion

3.1. Coating characterization

The SMF was characterized by scanning electron microscopy (SEM) before and after coating with polyPBA (Fig. 2). In contrast to the relatively smooth surface of the original SMF, the surface of the fiber after coating with polyPBA was rough, indicating that polyPBA had been fixed on the surface of the fiber.

3.2. Optical reflectance spectra and performance

Fig. 3 shows normalized reflection spectra of the tapered optical SMF tip coated with polyPBA in glucose solutions of different concentrations at room temperature. The reflectance of air of the tapered optical SMF tip coated with polyPBA was set as the reference and each spectrum was normalized with the reference. The reflectance increases with increasing glucose concentration, as shown in Fig. 3(a). The peak reflectance has a nearly linear dependence on glucose concentration in the range of 0–60 mM (Fig. 3(b)) – an attractive feature for glucose measurement. The response of the fiber sensor is attributed to the polyPBA layer, which swells when it interacts with glucose (reversibly), leading to a decrease in refractive index and higher reflectance. Although with increasing solution concentration the refractive index of the solution is increased with increasing glucose concentration (which would be expected to decrease reflectance), the value is negligible compared with the much larger increase resulting from the interaction between polyPBA and glucose. After each measurement, the fiber sensor is prepared for another measurement by rinsing with phosphate buffer solution (PBS, pH = 7.4) and drying.

3.3. Reusability and reproducibility of the sensor

We next assessed the reusability and reproducibility of the sensor by comparing the response of the sensor in PBS solutions containing different concentrations of glucose with the response in a pure PBS solution. The sensor tip was rinsed with PBS solution after each measurement. As shown in Fig. 4(a), after measurements in glucose solutions (5 mM or 20 mM) followed by washing of the sensor tip, the reflection spectra were nearly identical when the sensor was immersed in PBS only, thus suggesting the PBA fiber sensors are robust and reusable. Also, the reflectance for the 20 mM glucose solution was higher than

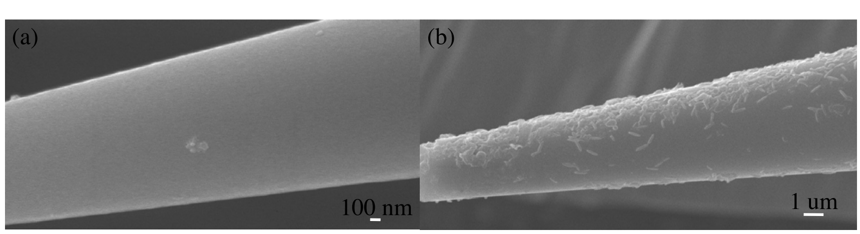

Fig. 2. (a) SEM image of the bare optical fiber before coating with polyPBA. (b) SEM image of the same fiber after coating with polyPBA.