Non-close packed photonic crystal hydrogel for glucose detection

Yunhe Lan*1

1Department of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing, 100081, China
2Corresponding author’s e-mail: lanyh93@163.com

Abstract. Based on the importance of fast and non-invasive detection technology of glucose monitoring, a glucose sensor based photonic crystal hydrogel material was prepared. The phenylboric acid was the glucose recognition molecule and the three-dimensional non-close packed array was the signal transformation structure. The experimental results show that the recognition behavior of the hydrogel is shown in the form of diffraction wavelength. As the glucose concentration increases from 0 mol /L to 50 mM, the blue shift of the diffraction wavelength occurs at 10 nm, showing a good sensing property.

1. Introduction

Diabetes is one of the most important diseases threatening human health in the world and monitoring glucose real-time is of great significance for disease control and effective treatment [1]. To avoid discomfort of blood collection, non-invasive glucose detection technology become a research hotspot at present[2].

Photonic crystals (PCs) are emerging optical materials, which are increasingly used in analytical chemistry[3]. The detection principle of PC sensor is that the structure of the functionalized PC will change after absorbing the target compound, which will cause the diffraction wavelength to change[4]. Introducing PC technology into glucose sensitive hydrogel materials can develop fast responsive sensing materials. The team of Yukikazu Takeoka modified the phenylboric acid on the reverse opal hydrogel skeleton and the detected glucose concentration by the diffraction peak of the photonic crystal[5]. Glucose oxidase or phenylboronic acid functional monomer is immobilized on the hydrogel network structure in the Asher Laboratory. Because of the non-close packed three-dimensional (3D) colloidal crystal array (CCA) embedded in the hydrogel, recognition of glucose on the base causes the volume change of the hydrogel, resulting in the change of lattice parameters of colloidal crystals and the appearance of the optical band gap. Optical sensing of glucose has been realized[6]. Although the introduction of photonic crystals provides a good platform for the development of glucose sensors, these PC sensing materials still have some problems, such as low selectivity.

In this study, we have introduced non-close packed photonic colloidal hydrogel for glucose detection. The recognition response of hydrogels to glucose is manifested by the movement of optical forbidden band in photonic crystal structure, and a fast and highly selective glucose response is achieved.

2. Materials and methods

2.1. Materials
Acrylamide (AM), acrylic acid (AA), N, N’-methylene bisacrylamide (BIS), polystyrene (PS), 2,2-diethoxyacetophenone (DEAP), dimethyl sulfoxide (DMSO), 3-acrylamidophenylboronic acid (3-APBA), 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC), glucose, NaOH and ion exchange resin were purchased from J&K Chemicals. Deionized water (Aquapro) was used as solvent.

2.2. Preparation of non-close packed array
Here, 0.4 g AM (4.54 mmol), 10 mg BIS (0.065 mmmol), 5 uL DEAP, 45 uL DMSO, 2 mL PS (100 nm, 1-10 wt%) and 1.5 g ion exchange resin were added to a 5 mL centrifugal tube. The mixture suspension, shown in figure 1. a and c, was shaken on shaking bed for 30 minutes at room temperature. 50 uL above liquid was injected by a liquid transfer gun into the void of the glass-tape-glass structure (thickness=125, 250, 375 um, Figure 1. b). The array was polymerized by the ultraviolet cross-linking instrument for 1 hour and then taken out for drying.

Figure 1. (a) The mixture suspension with 100nm 10%wt PS, (b) Non-close packed functionalized hydrogel with thickness of 125, 250, 375 um, (c) The mixture suspensions with 1-10 wt% PS.

2.3. Preparation of functionalized hydrogel
The 0.36 g AM (5.04 mmol), 38.5 uL AA (5.56 mmol), 10 mg BIS (0.065 mmmol), 2.8 uL DEAP, 25.2 uL DMSO and 2 mL deionized water were added to a 5 mL centrifugal tube. The mixture was sonicated for 5 min and deoxygenated by nitrogen bubbling for 10 min. According to above method of hydrogel polymerization, 50 uL mixture was injected into the void of the glass-tape-array structure and a layer hydrogel with carboxylic group was obtained. Then 3-APBA (25mM) was grafted on the hydrogel through crosslinking agent EDC (25mM) in ice bath for 7h.

2.4. Characterization
The hydrogel structural was characterized by a Scanning Electron Microscope (SEM, Quanta FEG 250, FEI). The optical diffraction of non-close packed array and hydrogel was characterized using an ultraviolet spectrophotometer (Avaspec-2048TEC, Avantes).

3. Results and Discussion

3.1. The structural characterization of hydrogel
Figure 2 shows a SEM image of the photonic crystal hydrogel demonstrating the non-close packed structure and uniform orderly distribution throughout the array.

3.2. Preparation of non-close packed photonic crystal hydrogel
The non-close packed array consisting of 100nm PS colloidal particles was embedded in hydrogel by polymerizing mixture of dispersed uniformly PS and uncharged monomer AM. To ensure diffraction peak within the detection range, the mass fraction of PS and hydrogel thickness were researched. Here, Figure 3.a shows the diffraction peak of mixture suspensions with 1-10 wt% PS. With the decrease of
PS mass fraction, the number of microspheres decreased causing the spacing of microspheres in the array increases and the diffraction peak shifts red. The structure color of suspension changes from dark blue to light blue. Figure 1.b shows the structure color of three non-close packed functionalized hydrogels with thickness of 125, 250, 375 um and Figure 3.a shows the diffraction peak of them. The hydrogel with 375um has no obvious color and has a larger diffraction peak, the hydrogel with 125um has no diffraction peak because the ordered structures were destroyed in small void. Thus, 10wt% PS and 250um hydrogel thickness were best choices.

![Figure 2. SEM images of the non-close packed PC hydrogel.](image)

![Figure 3. (a) The diffraction peak of mixture suspensions with 1-10 wt% PS, (b) The diffraction peak of non-close packed functionalized hydrogel with thickness of 125, 250, 375 um.](image)

![Figure 4. The diffraction peak of non-close packed PC hydrogel.](image)
3.3. Sensing glucose by hydrogel
The glucose recognition molecule is phenylboronic acid. At high ionic strength, the hydrogel responds to glucose, and crosslinking of phenylboric acid and glucose causes the shrink of hydrogel and the blue shift of diffraction peak[7]. When the hydrogel was immersed in glucose range from 0 to 50 mM, the blue shift of diffraction peak was observed (Figure 4) after equilibration for 15 minutes, but the structure color did not change significantly.

4. Conclusions
Mixed PS emulsions and uncharged monomer AM, BIS as crosslinking agent and DEAP as photoinitiator, were polymerized into three dimensional non-close packed hydrogel, and then functionalized that the phenylboric acid was grafted onto the hydrogel skeleton to obtain glucose sensing material. By controlling the mass fraction of PS emulsion and the thickness of the hydrogel, the distance of the microspheres and the range of diffraction peaks can be designed. If the response range is large, rapid naked eye detection can be realized. The blue shift of hydrogel in 0-50 mM glucose is 10 nm and needs further optimization.

Acknowledgments
This research was supported by the National Natural Science Foundation of China.

References
[1] Skyler, J.S., Oddo, C. (2002) Diabetes Trends in the USA. Diabetes/Metabolism Research and Reviews, 18: S21-S26.
[2] Yan, Z.Q., Xue, M., He, Q., Lu, W., Meng, Z.H., Yan, D., Qiu, L.L., Zhou, L.J., Yu, Y.J. (2016) A non-enzymatic urine glucose sensor with 2-D photonic crystal hydrogel. Anal Bioanal Chem, 408: 8317-23.
[3] Thammakhet, C., Thavarungkul, P., Kanatharana, P. (2011) Two-Dimensional Photonic Crystal Chemical and Biomolecular Sensors. Analytica Chimica Acta, 695: 105-112.
[4] Holtz, J.H., Holtz, J.S.W., Munro, C.H., Asher, S.A. (1988) Intelligent Polymerized Crystalline Colloidal Arrays: Novel Chemical Sensor Materials. Analytical Chemistry, 70: 780-791.
[5] Nakayama, D., Takeoka, Y., Watanabe, M., Kataoka, K. (2003) Simple and Precise Preparation of a Porous Gel for a Colorimetric Glucose Sensor by a Templating Technique. Angewandte Chemie International Edition, 42: 4197-4200.
[6] Asher, S.A., Alexeev, V.L., Goponenko, A.V., Sharma, A.C., Lednev, I.K., Wilcox, C.S., Finegold, D.N. (2003) Photonic Crystal Carbohydrate Sensors: Low Ionic Strength Sugar Sensing. Journal of the American Chemical Society, 125: 3322-3329.
[7] Xue, F., Meng, Z.H., Qi, F.L., Xue, M., Wang, F.Y., Chen, W., Yan Z.Q. (2014) A 2-D photonic crystal hydrogel for selective sensing of glucose. Analyst, 139: 6192-6.