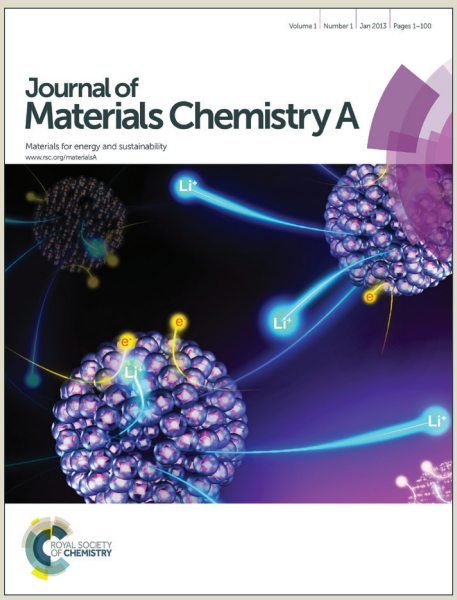
Journal of Materials Chemistry A

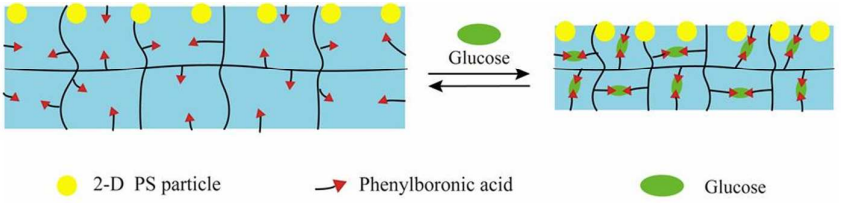
Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/materialsA

A novel 2-D photonic crystal hydrogel for selective glucose sensing is produced by attaching 2-D colloidal array onto the phenylboronic acid modified hydrogel.



Journal Name

RSCPublishing

ARTICLE

2-D photonic crystal hydrogel for the selective sensing of glucose

Cite this: DOI: 10.1039/x0xx00000x

Fei Xue, Zihui Meng*，Fengyan Wang, Qiuhong Wang, Min Xue*, Zhibin Xu

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

A novel 2-D photonic crystal (PC) sensing material for the visual detection of glucose with high selectivity at physiological ionic strength (150 mM) is developed. A monolayer polystyrene crystalline colloidal array (CCA) is embedded in a phenylboronic acid (PBA) functionalized hydrogel film to diffract light to sensitively report on the hydrogel surface area. This 2-D PC sensor is superior to the previously reported 3-D PC sensors due to its fast preparation and simple detection. The binding of glucose would increase the cross-linking of the hydrogel that could shrink the hydrogel to increase the Debye diffraction ring diameter. At 150 mM of physiological ionic strength, the 2-D PC sensor exhibits significant sensitivity for glucose across the entire human physiologic glucose range. Additionally, the 2-D PC sensor shows high selectivity for glucose rather other sugars (fructose and galactose). The diffraction color change of the 2-D PC sensor can be observed. For validation, the prepared 2-D PC hydrogel sensor is applied for the sensing of glucose in the artificial tear.

1 Introduction

There is great interest in the development of chemical and biological sensors to visually determine concentration of species in aqueous environments.[1-4] The ideal sensing technology should be highly selective and appropriately sensitive to the analyte concentrations of interest. Among various sensing technologies, responsive photonic crystal hydrogels have attracted substantial attentions because of their visual diffraction signals and intelligent response to external stimuli.[4-8] Photonic crystals (PC) are highly ordered materials with periodicity on the order of the wavelength of light and Bragg-diffract visible light depending on the lattice spacing.[9,10] By incorporating the stimulus-responsive hydrogel into the 3-D PC structure, the constructed responsive PC could act as optical sensors for a variety of external stimuli.[8, 11-14] The volume change of the hydrogel in response to stimuli would be converted to the diffracted wavelength shift by a 3-D colloidal crystalline arrays (CCA) embedded in the hydrogel matrix.

Phenylboronic acid (PBA) functionalized hydrogels are well known as glucose-responsive hydrogels due to their affinity to diol-containing molecules.[15-17] The interaction of immobilized PBA in hydrogel matrix with glucose would lead to volumetric changes which would make the hydrogel a candidate for glucose sensing. Thanks to the low cost of the self-assembly methods, 3-D CCA has been utilized for the formation of PC structures.[4, 18, 19] Intensive research efforts have been conducted to prepare glucose-responsive 3-D PC hydrogels via a combination of 3-D CCA and PBA modified hydrogel. In their pioneer work, Asher et al. polymerized acrylamide around charge-stabilized 3-D CCA to form a polymerized CCA (PCCA), followed by modification with PBA groups.[20-22] Due to the dielectric periodicity of the CCA and Bragg's law, this PCCA hydrogel would diffract light of certain frequencies. However, these hydrogel-CCA composites require the use of non-ionic hydrogel precursors to avoid disordering the charge-stabilized 3-D CCA, thus limiting the ionic monomers and increasing the modification steps of binding PBA moieties to the hydrogel. The follow-up studies by Braun et al.[17] and Takeoka[23, 24] employed PBA functionalized inverse opal PC hydrogels for glucose sensing using dried 3-D close-packed CCA as templates. These responsive PC hydrogel sensors were sensitive to glucose regarding the physiological concentrations. Unfortunately, the self-assembly of 3-D CCA is time-consuming because it usually takes weeks to obtain the PC structure with a good order. Another disadvantage is that the selectivity is poor. In short, the tedium and time-consuming preparation process and poor selectivity limit the application of these 3-D PC hydrogels for glucose-sensing application. Thus, it is critical to develop new glucose-sensing PC sensors which are easy to prepare and exhibit high selectivity.

Most recently, a fast fabrication of 2-D CCA at the air/water interface was reported.[25, 26] This self-assembly approach can produce a continuous 2-D CCA monolayer (>280 cm^2) in 2 min. Compared with traditional 3-D CCA self-assembly, this air/water interface self-assembly method is much simpler and faster. Some pioneer studies have shown that 2-D CCA is easy to be incorporated into hydrogels.[27, 28] Moreover, besides the diffraction wavelength detection by spectroscopy, the intense forward Debye diffraction could be used as a more convenient way to monitor the 2-D lattice spacing.[29] Thus, it would be desirable to combine 2-D PC with glucose-responsive hydrogel to improve the fabrication and detection.

Herein, a new 2-D PC hydrogel for visual glucose sensing by attaching 2-D CCA monolayer on a PBA-modified hydrogel is reported in this paper. The volumetric change of hydrogel in response to glucose induces the neighboring particle spacing of the 2-D CCA change causing the Debye diffraction ring

diameter to alter. This sensor has the advantages of the fast preparation of 2-D CCA and the simple method of Debye ring diffraction readout. Most importantly, the 2-D PC hydrogel shows high selectivity towards glucose at physiological ionic strength (150 mM).

2 Experimental

Materials

Styrene was purchased from Sigma. Acrylic acid (AA), 1-propanol, 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC), 2-(cyclohexylamino)ethanesulfonic acid (CHES), glucose, fructose, and galactose were obtained from Aladdin Co. Ltd. Acrylamide (AM), 3-acrylamidophenylboronic acid (3-APBA), 2-hydroxethyl methacrylate (HEMA), potassium persulfate, N,N'-methylenebisacrylamide (BIS), 2,2-diethoxyacetophenone (DEAP), dimethyl sulfoxide (DMSO), NaOH were purchased from Acros Organics and used as received. Deionized water (Aquapro) was used for the experiment.

Preparation of 2-D CCA

The monodispersed polystyrene (PS) colloidal particles were synthesized according to a previously reported emulsion method.[32] Briefly, 70 g styrene, 2 g HEMA and 205 mL water were charged into a 500 mL flask. N_2 was bubbled for 40 min to remove O_2. Then the temperature was increased to 70 ℃. 0.11 g potassium persulfate in 5 mL water was added to the reaction solution to initiate the polymerization. The reaction was carried out at 70 ℃ overnight in a N_2 atmosphere. After repeated centrifugation and dispersion in deionized water, monodispersed PS colloidal particles with a diameter of 590 nm were obtained.

The PS colloid suspension at a concentration of 20 wt % and 1-propanol were mixed at a ratio of 3:1 in volume. Then about 20 μL of this suspension was slowly and smoothly layered onto the top of a water surface in a 10 cm diameter glass container to form a hexagonal close-packed 2-D monolayer CCA. To transfer the 2-D CCA onto a substrate, the 2-D CCA was picked up with a glass slide.

Preparation of glucose-responsive 2-D PC hydrogel

A poly acrylamide co acrylic acid (PAM-AA) hydrogel film was polymerized over the 2-D CCA on glass slides which utilized DEAP as a photoinitiator. A typical recipe contained 0.36g (5.04 mmol) of AM, 38.5 μL (0.56 mmol) of AA, 10 mg (0.065 mmol) of BIS, and 2 mL deionized water. This polymerization mixture was deoxygenated by nitrogen bubbling for 10 min. A 28 μL of a 10% solution of DEAP in DMSO (13.6 μmol of DEAP) was added to the AM-BIS-AA suspension. This mixture was layered onto a 2-D CCA on a glass slide. A glass slide (60 mm × 24 mm × 0.12 mm) was placed over the solution covering the 2-D CCA. The polymerization was initiated with 365 nm UV illumination for 1 h at room temperature. The 2-D particles were embedded within the PAM-AA hydrogel. The resulting 2-D PC PAM-AA hydrogel film was peeled from the glass slide and washed with deionized water.

The resulting 2-D PC PAM-AA hydrogel was further modified by EDC crosslinking reaction to incorporate phenylboronic acid groups into the hydrogel matrix. The 2-D PC PAM-AA hydrogel was incubated in a solution containing 25 mM EDC and 25 mM 3-APBA for 3 h. The 3-APBA was linked to the hydrogel by reacted with AA group using EDC as a cross-linker. The obtained glucose-sensitive 2-D PC hydrogel were repeatedly washed with deionized water.

Characterization

Structural characterizations of the 2-D CCA and the resultant 2-D PC hydrogel were performed using SEM (Quanta FEG 250, FEI) after sputter-coating a layer of gold. The reflectance spectra from the 2-D PC hydrogel sensor were obtained using a fiber optic UV-vis spectrometer (Avaspec-2048TEC, Avantes) with a 30° measurement angle between the probe and the normal to the 2-D PC.

The Debye diffraction ring was utilized to characterize the particle spacing of 2-D PC hydrogel. Typically, a violet laser (405 nm) was illuminated on the 2-D PC hydrogel at a normal angle. At normal incidence, the diffracted light on the screen perpendicular to the laser reflects the 2-D particle spacing and ordering by showing a round ring. The 2-D CCA particle spacing, d, was calculated through the modified Bragg diffraction equation using the ring diameter, D, and the distance of the screen to the 2-D PC hydrogel sample, h.

To characterize the response of the 2-D PC PAM-AA hydrogel and 2-D PC glucose-sensitive hydrogel to pH change, the hydrogel sensors were immersed in 50 ml buffer solution with different pH from 2 to 10.5 at room temperature. After 5 min, the diffraction wavelength or the Debye diffraction ring was recorded.

The optical responses of the 2-D PC hydrogel films to sugars in low and high ionic strength condition were measured in a CHES buffer (9.0). For low ionic strength buffer, 10 mM CHES buffer solution at pH 9.0 was made by dissolving CHES (1.036g) in 450 mL water, followed by titration to pH 9.0 with NaOH (1 M) and dilution to 500 mL. The 2-D hydrogel film should be soaked in a buffer with different concentrations of sugar for 5 min before each Debye ring measurement. High ionic strength buffer (pH 9, ionic strength ~ 150 mM) was made by mixing CHES (7.5 mmol), NaCl (12 mmol) in deionized water to make a 50 mL solution, followed by titration to pH 9.0 with NaOH (1 M) and dilution to 100 mL with deionized water.

The photograph of the 2-D PC hydrogel sensors were taken using a digital camera (Sony, Cyber-shot DSC-N2) at an angle of ~30° between the light source/camera and the 2-D PC hydrogel normal. The 2-D PC hydrogel sensors were placed on a silver mirror.

3. Results and discussion

3.1 Fabrication of glucose-responsive 2-D PC hydrogel

Glucose-responsive 2-D PC hydrogel was prepared by attaching 2-D CCA of PS particles with a diameter of 590 nm onto the surface of poly acrylamide co acrylic acid (PAM-AA) hydrogels. Glucose recognition sites were then created by the chemical modification of the 2-D PC PAM-AA hydrogel with PBA derivatives. As illustrated in Figure 1a, the fabrication process was divided into 4 steps. 1) A well-ordered 2-D CCA of PS particles on a glass slide; 2) A pre-polymerization solution containing acrylamide (AM), acrylic acid (AA), N,N'-methylenebisacrylamide (BIS), and 2,2-diethoxyacetophenone (DEAP) were infiltrated into the 2-D CCA, and a glass slide (60 × 24 mm) was then placed on top of the 2-D CCA; 3) Polymerization was initiated by UV light and the resulting 2-D

CCA-embedded PAM-AA hydrogel film was peeled from the glass slide and rinsed with a large amount of water; 4) PAM-AA hydrogel was functionalized by PBA groups to afford the glucose-responsive 2-D PC hydrogel.

For the preparation of the 3-D PC glucose sensitive hydrogel, the hydrogel-CCA composites require the non-ionic hydrogel precursors to avoid disordering the charge stabilized 3-D CCA, which would limit the ionic monomers and increase the modification steps to bind the hydrogel with the functional moieties. Usually, two steps are needed to modify the hydrogel with PBA derivatives. For the 2-D PC hydrogel fabrication, the 2-D CCA fabrication was decoupled from the responsive hydrogel synthesis. This decoupling would allow us to directly use AA monomer to fabricate hydrogels followed by only one modification step for PBA groups linking. As shown in Figure 1b, PBA group was linked to the PAM-AA hydrogel by a site-specific reaction between the 3-APBA and the prepositioned AA monomer in the hydrogel.

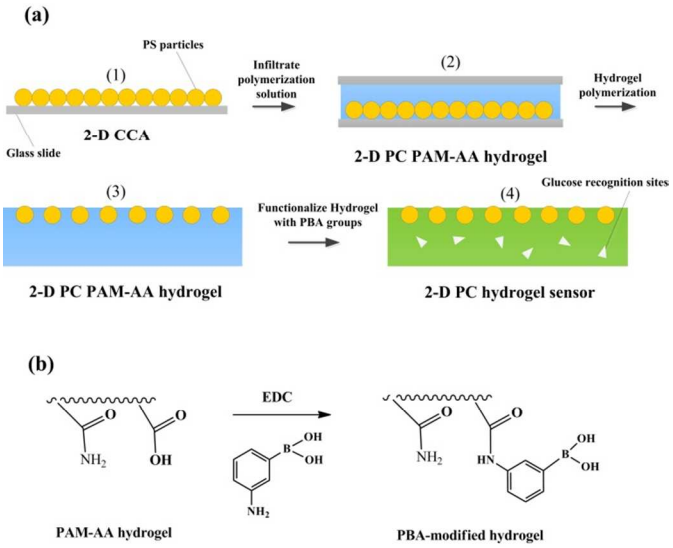


Figure 1. (a) Fabrication of a glucose-responsive 2-D PC hydrogel. (1). 2-D CCA on a glass slide. (2). Infiltrate pre-polymerization solution into the 2-D CCA and initiate the polymerization by UV light. (3). Separate the 2-D PC hydrogel film from the glass slide and wash it with water. (4). Functionalize the 2-D PC hydrogel with PBA groups. (b) The chemistry of coupling PBA recognition groups to the hydrogel matrix.

To obtain a well-ordered 2-D CCA, monodispersed PS particles with the diameter of 590 nm were prepared and self-assembled on an air/water interface. This self-assembly approach can produce a continuous 2-D CCA monolayer (>80 cm^2) in 1 min. Compared with traditional self-assembly of 3-D CCAs, the air/water interface self-assembly method is easier and faster. Take Asher's PCCA glucose sensor as an example. In order to prepare well-ordered non-close-packed 3-D CCA, the self-assembly process took about at least 2 to 3 weeks by dialyzing the PS particles against water.[20-22] More than one week was needed to prepare 3-D close-packed CCA templates of colloidal particles in Braun and Takeoka's research work. [17, 23, 24] What's more, the etching of the 3-D CCA templates took about 1 to 2 days. Thus, our 2-D CCA self-assembly significantly improves the 2-D PC hydrogel preparation time. PS particles Figure 2a shows a SEM image demonstrating the high ordering of the close-packed hexagonal 2-D CCA of PS spheres on a glass slide. Figure 2b shows that during hydrogel polymerization the space between neighboring particles was filled with hydrogel polymer and the ordering of the 2-D CCA was not degraded by the polymerization and transfer process. The cross-sectional view of the 2-D PC hydrogel film in Figure 2c further demonstrates that the 2-D CCA is a monolayer mounted on the top of the hydrogel.

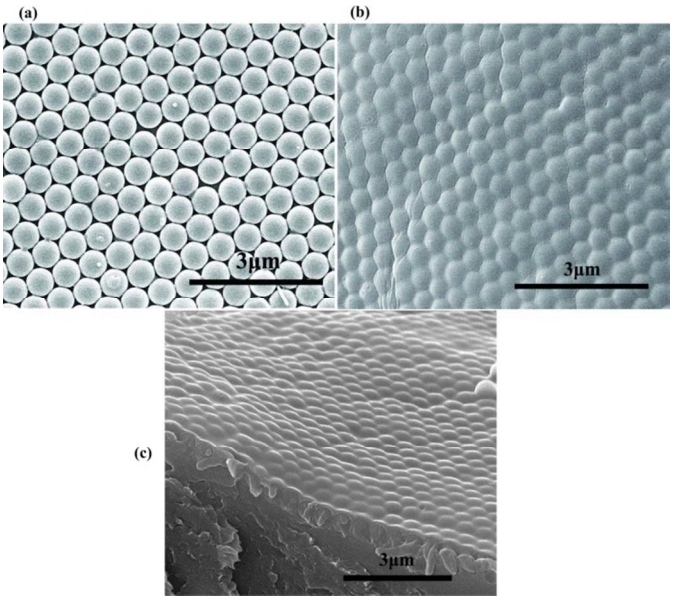


Figure 2. SEM images of (a) PS 2-D CCA on a glass slide, (b) surface of the 2-D PC hydrogel with PS 2-D CCA monolayer embedded, and (c) abraded hydrogel showing PS 2-D CCA embedded in the hydrogel film.

3.2 Characterization of the 2-D CCA diffraction

Most recently, a much easier way has been developed to characterize the 2-D CCA diffraction by measuring the forward Debye diffracted ring diameter. As shown in Figure 3a, at normal monochromatic incidence, the forward diffracted light of the 2-D CCA forms a ring on a screen. The Debye diffraction of the 2-D PC follows: $\sin\alpha = 2\lambda/\sqrt{3}d$, where α is the forward diffraction angle of the Debye diffraction, λ is the incident wavelength, and d is the nearest neighboring particle spacing. The forward diffraction angle, α, can be obtained by calculation: $\alpha = \tan^{-1}(D/2h)$, where h is the distance between 2-D CCA and the screen, D is the Debye ring diameter. Therefore, the 2-D CCA particle spacing could be determined by measuring the Debye ring diameter D. Figure 3b shows the experimental setup to monitor the diffraction ring diameter in our research. For 2-D PC hydrogel characterization, the volumetric change of the hydrogel leads to the particle spacing of the 2-D CCA change since the monolayer 2-D CCA has been attached to the hydrogel surface. In other words, the volume change of hydrogel correlates with the change of particle spacing which could be determined by the Debye ring diameter. Expensive visible fiber optic spectrometer was always utilized to characterize the diffraction shift of the 3-D PC hydrogels. The diffraction detection operation method is relatively complex because it needs darkroom to avoid the interference of the light in the environment. Our experimental setup only needs a ring stand with a laser pointer. Sometimes, the diffraction wavelength cannot be measured by a visible spectrometer if the wavelength is in invisible region. However, we can still detect

the 2-D PC hydrogel particle spacing by monitoring the Debye diffraction ring. Therefore, compared with traditional spectrometer measurement of the diffraction wavelength of 3-D PC, Debye ring detection method would be much cheaper and easier. In the following research, Debye ring measurement method was utilized to characterize the 2-D PC hydrogel responses.

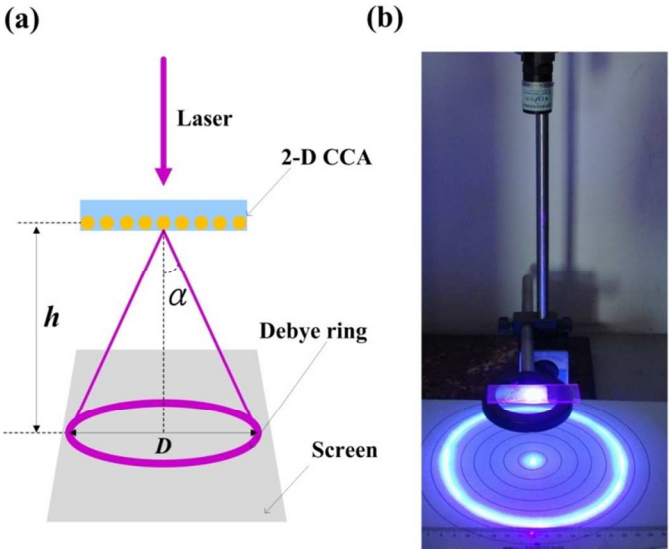


Figure 3. (a) Schematic illustration of the Debye diffraction ring pattern. (b) Photograph showing the experimental setup to measure the Debye diffraction ring of 2-D CCA under a 405 nm incidence laser wavelength.

3.3. Characterization of PBA modification of hydrogel

The fact of the PBA modification step is that carboxyl groups of AA in the hydrogel were replaced by PBA derivatives (Figure 1b). Both carboxyl group (pKa ~4.3) and PBA group (pKa ~9) are weak acids that hydrolyze in aqueous solution depending on their pKa. This hydrolysis would ionize these acidic groups and immobilize counter ions inside the hydrogel resulting in an osmotic pressure, which swells the hydrogel. This indicates that the 2-D PC hydrogels should exhibit different pH response properties before and after the PBA modification. Figure 4 demonstrates the pH dependence of the particle spacing of the 2-D PC PAM-AA hydrogel and PBA-modified hydrogel. It could be observed that the pH response of the PBA-modified hydrogel shifts to higher pH direction. PAM-AA hydrogel swells significantly near pH4.25, while the most sensitive pH response of the PBA-functionalized hydrogel occurs near pH9. To some extent this pH response variation proves that PBA groups were successfully coupled to the hydrogel matrix.

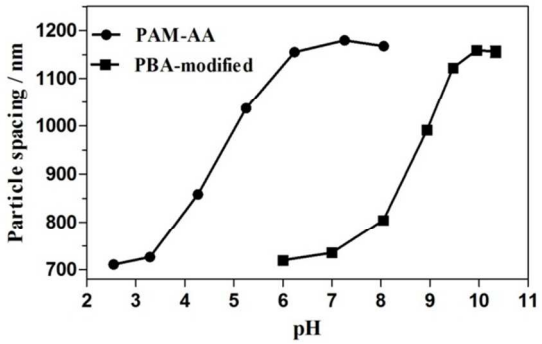


Figure 4. pH dependence of the particle spacing of the 2-D PC hydrogel in phosphate buffer (10 mM).

3.4. Selective sensing of glucose by 2-D PC hydrogel

The response of the 2-D PC hydrogel to glucose was studied in 150 mM CHES buffer (pH9) which is close to the physiological fluids ionic strength at room temperature. As shown in Figure 5a, the hydrogel sensor shrinks with increasing the glucose concentration. The 2-D particle spacing decreases from 843 to 830 nm when glucose concentration increases to 0.1 mM. When glucose concentration increases to 10 mM, the particle spacing decreases to 775 nm. The 2-D PC hydrogel sensor exhibited the sensitivity for glucose across the entire human physiologic glucose range. Moreover, the diffraction color of the 2-D PC hydrogel sensors shifts from red to yellow, and then to green-blue with increasing glucose concentration (Figure 5a inset). We can visually detect 0.1 mM glucose since the diffraction color would change from red to orange. The most abundant monosaccharides in physiological fluids are fructose and galactose in addition to glucose. We used fructose and galactose as controls to investigate the selectivity of the 2-D PC hydrogel sensor for glucose. The control response experiments showed that fructose and galactose both swell the 2-D PC hydrogel and increased the particle spacing (Figure 5b). The swelling of the 2-D PC hydrogel also leads diffraction color change (see ESI). In order to make the diffraction wavelength of the 2-D PC hydrogel in control experiments is in the visible region, we adjust the angle between light source/camera and the swollen 2-D PC hydrogel normal at ~ °40. Now, only glucose shrinks the 2-D PC hydrogel while other sugars swell the hydrogel which means that our 2-D PC hydrogels exhibit high selectivity for glucose.

PBA can reversibly bind cis-1,2 or cis-1,3 diols of saccharides, e.g. glucose, to form a five- or six-membered boronic cyclic ester in aqueous media. The saccharide binding to PBA induces the formation of boronate anions, which results in a Donnan potential, which give rise to an osmotic pressure, which swells the 2-D PC hydrogel. However, the shrinking response to glucose derived from the interesting phenomenon that while most physiological relevant sugars bind to boronic acid as monobidentate complexes, glucose has the unique property to be involved in a bis-bidentate glucose-boronic acid complex through its furanose form (Figure 5c). As shown in Figure 5d, this bis-bidentate complex increases the cross-linking which shrinks the hydrogel.

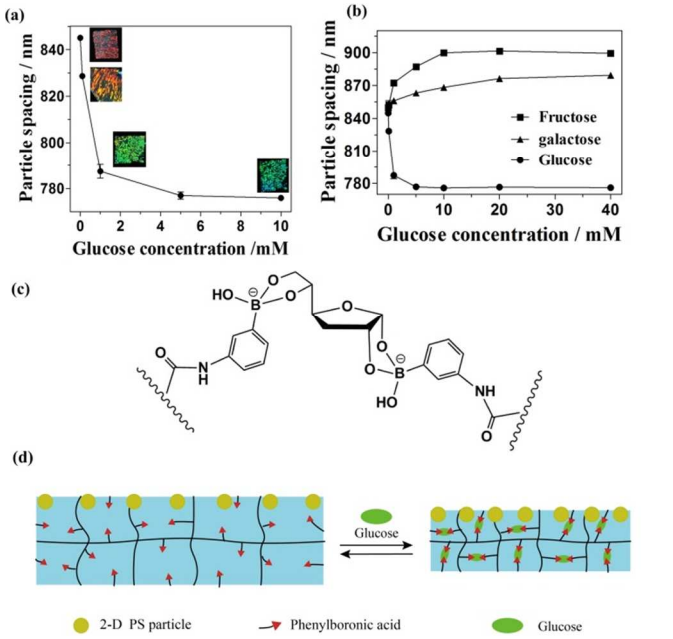


Figure 5. (a) Dependence of the particle spacing of the 2-D PC hydrogel on glucose concentration in CHES buffer (ionic strength 150 mM, pH9). Inset showed the diffraction color of the 2-D PC hydrogels. (b) The comparison of the 2-D PC hydrogel responses to glucose, fructose and galactose in CHES buffer (10mM, pH9). (c) Bis-bidentate glucose-boronate complexation with the furanose form of glucose. (d) Scheme of the shrinking response of 2-D PC hydrogel response to glucose.

Most 3-D PC glucose-responsive hydrogels based on PBA recognition motif swell in response to glucose.[17,20,23,30] For example, the glucose-sensitive inverse opal hydrogels prepared by Braun's group swelled in response to glucose. For another example, the PC hydrogel of Takeoka's group also showed swelling response in glucose aqueous solution. All these PC hydrogel sensors do not have a desirable selectivity for glucose because other sugars also swell the hydrogel. The reason would be that the PBA recognition groups distributed in hydrogel matrix are not dense enough so that the distance between two neighboring PBA group is too far to form bis-bidentate complexes with glucose. In this case, only monobidentate complexes form between glucoses and PBA moieties which swell the hydrogel, which performs like other sugars. For previous 3-D PC hydrogel glucose sensors, the PCCA utilized polymerization of a relatively diluted polyacrylamide hydrogel inside a charge-stabilized CCA, and then it was functionalized with PBA moieties through two steps.[20] This diluted hydrogel matrix and multistep modification procedure limit the PBA group concentration in hydrogel. Contrarily, 2-D PC hydrogel requires only one modification step to couple PBA to the hydrogel matrix. The concentration of PBA is easier to be controlled by varying the prepositioned AA monomer concentration. For instance, in the PBA-modified 2-D PC hydrogel, the ratio of PBA/AM would be about 1:9 if all the prepositioned AA groups were replaced by PBA during the modification step. Taken together, our 2-D PC hydrogel has simplified the fabrication procedure and meanwhile improved the selectivity to glucose.

3.5. Ionic strength dependence of response of 2-D PC hydrogel sensor

The ionic strength of the aqueous solution strongly affects the volumetric state of the charged hydrogel. As shown in Figure 6a, the CCA particle spacing decreases as the ionic strength increases by varying the concentration of NaCl in pH 9 CHES buffer solutions. This is because higher ionic strength screens the Donna potential due to ionization of PBA.[17] The distance between neighboring PBA groups would increase as the hydrogel swells by decreasing the aqueous solution ionic strength. We assume that if the neighboring PBA group distance is too far to form the bis-bidentate complex with glucose, the response mechanism would change and glucose would swell the hydrogel. As described above, our 2-D PC hydrogels selectively sense glucose by forming the bis-bidentate complex because the hydrogels are in shrinking state at physiological ionic strength as shown in Figure 5. To further prove our assumption, the response of the 2-D PC hydrogels to glucose and sugars were investigated at low ionic strength (10 mM). As shown in Figure 6b, all the sugars swell the hydrogel including glucose. Because the fructose and galactose have higher affinity constants with PBA than glucose,[31] the 2-D PC hydrogel exhibited higher sensitivity for fructose and galactose (Figure 6b). The results demonstrate that the 2-D PC hydrogel would response to glucose with two different mechanisms depending on the ionic strength condition, and physiological ionic strength favors the selectivity for glucose.

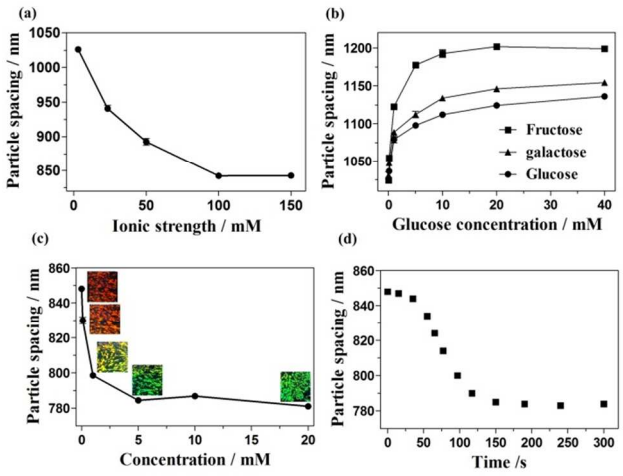


Figure 6. (a) Ionic strength dependence of the 2-D PC hydrogel in CHES buffer (pH9). (b) The comparison of the 2-D PC hydrogel responses to glucose, fructose and galactose in low ionic strength buffer (10 mM, pH9). (c) Glucose concentration dependence of the 2-D PC hydrogel in pH adjusted tear fluid. (inset) Diffraction color changes from red to green with increasing glucose concentration. (d) Kinetic of glucose sensing of the 2-D PC hydrogel for 10 mM glucose in artificial tear-fluid (pH was adjusted to pH9).

3.6. Visual detection of glucose in artificial tear fluid by 2-D PC hydrogel

We also investigated the response of the 2-D PC hydrogel sensor to glucose in an artificial tear-fluid prepared according to the Geigy Scientific Tables.[22] The pH of the artificial tear-fluid was adjusted to pH9.0. Although the proteins in the article tear fluid, such as albumins, γ-globulins and lysozyme, might interfere with the glucose sensing. The results shown in Figure 6c demonstrate that the 2-D PC hydrogel sensor response to glucose in artificial tear fluid in the same way as it is in the

CHES buffer shown (Figure 5a). The color changes are bright and visually evident, as seen in the inset of Figure 6c.This result demonstrates the feasibility of sensing glucose in tear fluid by 2-D PC hydrogel sensor. We also studied the swelling kinetics of the 2-D PC hydrogel sensor upon glucose binding. The particle spacing change of the 2-D PC to 10 mM glucose was recorded at different time. As shown in Figure 6d, 2-D PC hydrogel exhibited rapid response to glucose and reached binding equilibrium within 3 min.

4. Conclusions

We demonstrated a novel glucose-responsive PC hydrogel with high selectivity at physiological ionic strength by attaching monolayer 2-D CCA to PBA-modified hydrogel. The fast fabrication approach for 2-D CCA strongly improves the preparation of the PC hydrogel. A simpler method was utilized to characterize the diffraction response of the 2-D PC hydrogel by detecting the Debye diffraction ring. The volumetric change was sensitive regarding glucose binding due to the PBA-glucose complexes. At high ionic strength, the formation of the bis-bidentate PBA-glucose complex was associated with an increasing hydrogel cross-linking, which shrunk the hydrogel volume, thus decreasing the 2-D CCA particle spacing on the hydrogel surface. Other sugars binded to PBA by a monobidentate mechanism which swelled the hydrogel. These materials responded to glucose at physiological ionic strengths and were selective in their mode of response for glucose over galactose, and fructose. The 2-D diffraction from this PC hydrogel sensor could allow the visual detection of glucose binding. Sensitive response to glucose in pH adjusted artificial tear fluid demonstrates the flexibility of the 2-D PC hydrogel. Thus, we developed a new PC sensing material for glucose which would be promising for the fabrication of in vivo glucose sensing.

Acknowledgements

This research was supported by NSFC (20775007, 21375009) and the National Basic Research Program of China (973 program No. 2012CB910603). The authors also thank Professor Sanford Asher and Dr. Jian-tao Zhang from Department of Chemistry, University of Pittsburgh, for their instruction of preparation of 2-D colloidal crystalline array technique.

Notes and references

School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing, China 100081
Zihui Meng, E-mail: m_zihui@yahoo.com
Min Xue, E-mail: minxue@bit.edu.cn

Electronic Supplementary Information (ESI) available: Dependence of the particle spacing of the 2-D PC hydrogels on fructose and galactose, and their diffraction color change. See DOI: 10.1039/b000000x/

1 J. H. Holtz, S. A. Asher, *Nature*, 1997, **389**, 829.
2 G. R. Hendrickson, M. H. Smith, A. B. South, L. A. Lyon, *Adv. Funct. Mater.*, 2010, 20, 1697.
3 Q. Cao, J. A. Rogers, *Adv. Mater.*, 2009, 21, 29.
4 J. Ge, Y.Yin, *Angew. Chem. Int. Ed.*, 2010, 26, 1492.
5 M. M. W. Muscatello, S. A. Asher, *Adv. Funct. Mater.*, 2008, 18, 1186.
6 E. Tian, J. Wang, Y. Zheng, Y. Song, L. Jiang, D. Zhu, *J. Mater. Chem.*, 2008, 18, 1116.
7 X. B. Hu, G. T. Li, M. H. Li, J. Huang, Y. Li, Y. B. Gao, Y. H. Zhang, *Adv. Funct. Mater.*, 2008, 18, 575.
8 C. Fenzl, S. Wilhelm, T. Hirsch, O. S. Wolfbeis, *ACS Appl. Mater. Interfaces*, 2012, 5, 173.
9 G. von Freymann, V. Kitaev, B. V. Lotsch, G. A. Ozin, Chem. Soc. Rev., 2013, 42, 2528.
10 L. González-Urbina, K. Baert, B. Kolaric, J. Pérez-Moreno, K. Clays, *Chem. Rev.*, 2011, 112, 2268.
11 K. Lee, S. A. Asher, *J. Am. Chem. Soc.*, 2000, 122, 9534.
12 J. D. Debord, L. A. Lyon, *J. Phys. Chem. B*, 2000, 104, 6327.
13 J. Shin, P. V. Braun, W. Lee, *Sens. Actuators, B*, 2010, 150, 183;
14 M. Xu, A. V. Goponenko, S. A. Asher, *J. Am. Chem. Soc.*, 2008, 130, 3113.
15 A. Kikuchi, K. Suzuki, O. Okabayashi, H. Hoshino, K. Kataoka, Y. Sakurai, T. Okano, *Anal. Chem.*, 1996, 68, 823;
16 A. Matsumoto, S. Ikeda, A. Harada, K. Kataoka, *Biomacromolecules*, 2003, 4, 1410.
17 Y. J. Lee, S. A. Pruzinsky, P. V. Braun, *Langmuir*, 2004, 20, 3096.
18 C. I. Aguirre, E. Reguera, A. Stein, *Adv. Funct. Mater.*, 2010, 20, 2565.
19 J. F. Galisteo-López, M. Ibisate, R. Sapienza, L. S. Froufe-Pérez, Á. Blanco, C. López, *Adv. Mater.*, 2011, 23, 30.
20 S. A. Asher, V. L. Alexeev, A. V. Goponenko, A. C. Sharma, I. K. Lednev, C. S. Wilcox, D. N. Finegold, *J. Am. Chem. Soc.*, 2003, 125, 3322.
21 V. L. Alexeev, A. C. Sharma, A. V. Goponenko, S. Das, I. K. Lednev, C. S. Wilcox, D. N. Finegold, S. A. Asher, *Anal. Chem.*, 2003, 75, 2316.
22 V. L. Alexeev, S. Das, D. N. Finegold, S. A. Asher, *Clin. Chem.*, 2004, 50, 2353.
23 D. Nakayama, Y. Takeoka, M. Watanabe, K. Kataoka, *Angew. Chem. Int. Ed.*, 2003, 42, 4197.
24 M. Honda, K. Kataoka, T. Seki, Y. Takeoka, *Langmuir*, 2009, 25, 8349.
25 J.-T. Zhang,; L. Wang, J. Luo, A. Tikhonov, N. Kornienko, S. A. Asher, *J. Am. Chem. Soc.*, 2011, 133, 9152.
26 J.-T. Zhang, L. Wang, D. N. Lamont, S. S. Velankar, S. A. Asher, *Angew. Chem. Int. Ed.*, 2012, 51, 6117.
27 J.-T. Zhang, L. Wang, X. Chao, S. A. Asher, *Langmuir*, 2011, 27, 15230;
28 J.-T. Zhang, N. Smith, S. A. Asher, *Anal. Chem.*, 2012, 84, 6416.
29 J.-T. Zhang, X. Chao, X. Liu, S. A. Asher, *Chem. Commun.*, 2013, 49, 6337.
30 Y. Liu, Y. Zhang, Y. Guan, *Chem. Commun.*, 2009, 14, 1867.
31 O. B. Ayyub, M. B. Ibrahim, R. M. Briber, P. Kofinas, *Biosens. Bioelectron.*, 2013, 46, 124.
32 C. E. Reese, S. A. Asher, *J. Colloid Interface Sci.*, 2002, 248, 41.

