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Fast response photonic crystal pH sensor based on templated photo-polymerized hydrogel inverse opal

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ABSTRACT

Polymer hydrogels can exhibit large reversible volume changes in response to external stimuli, and thus are regarded as excellent materials for chemical sensors. In this report, we demonstrate a mechanically robust and fast response photonic crystal pH sensor fabricated by templated photo-polymerization of hydrogel monomers within the interstitial space of a self-assembled colloidal photonic crystal. Throughout a rigorous optimization of the photo-polymerization, pH sensors showing a response time of less than 10 s upon a pH change were fabricated. Repeated pH changes revealed that the sensor has a long lifetime (>6 months) without degradation of the response time or reproducibility in pH-driven color change.

1. Introduction

Stimuli-responsive chemical sensors are of great importance for environmental, food, and biological applications. For sensing chemical stimuli, complicated electrical or optical detection strategies are often used which require sophisticated and expensive detection systems. Recently developed photonic crystal hydrogel sensor strategies which rely on the diffraction induced color change of the sensor are now however enabling the detection of the analyte molecules simply with the naked eye [1]. A common detection mechanism is based on a volume change of hydrogel exerted by Donnan potential between the analyte ions and their receptor which is covalently bound to the hydrogel building block. In order to compensate the local ion inhomogeneity, there is influx of water molecules to the hydrogel. The optical readout of such hydrogel structures is because they are imprinted with a periodic structure, forming a so-called photonic crystal, and the volume change in the periodic structure results in the color change of the sensor. Such color is often called 'structural color' due to the origin of color. Important advantages of the hydrogel photonic crystal sensor are that relatively simple optical detection techniques are possible, and that a wide variety of analytes including protons [2–5], metal ions [6], glucose [7–9], and volatile organic compounds (VOC) [10], to name a few have been successfully detected using such sensors. Much of the pioneering work on hydrogel photonic crystal sensor was first reported by Holtz and Asher [1]. They developed the polymerized crystalline colloidal array (PCCA) concept, which relies on highly charged polystyrene (PS) colloids to form a crystalline array within a cross-linkable aqueous medium. The sensing moiety, which induces volume change upon exposure to the analyte, is polymerized into the hydrogel [3]. Asher also used highly charged silica particles as the PCCA template, and compared the pH and ethanol sensing capability before and after etching silica particles [5]. In this study, the detailed sensing mechanism was investigated from thermodynamic standpoint, in which hydrogel swelling was well described by thermodynamic interaction between polymer/solvent and Donnan equilibrium of the bound charge as well. Lyon has reported on hydrogel microspheres made from *N*-isopropylacrylamide (NIPAM) and acrylic acid (AA), which form a temperature and pH responsive fluidic colloidal crystalline array in water [2]. Another novel approach is the inverse opal-type hydrogel photonic crystal sensor. Takeoka and coworkers demonstrated various inverse opal sensors fabricated from the silica colloidal crystal template. After polymerization of hydrogel within the interstitial space of the colloidal crystal, silica template was removed by hydrofluoric acid, and the remaining inverse opal hydrogel exerted a variety of sensing phenomena depending on the chemical equilibrium between the analyte and the bound receptor

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[11,12]. Braun et al. reported on the fabrication of pH and glucose responsive inverse opal hydrogel sensors using a polystyrene based colloidal crystal template [4,7,13].

In spite of relative simplicity and versatility of hydrogel photonic crystal sensors, the slow response time due to a hindered diffusion of the analyte molecule through the hydrogel often limits their practical applications [14,15]. We previously showed that the use of inverse opal hydrogel structure under an optimized fabrication strategy can significantly improve the response time of a hydrogel based pH sensor [4]. Asher recently reported an improved response kinetics of glucose sensor [9]. Here, we apply a polymerization method for forming the hydrogel; photo-polymerization is advantageous in that it enables fine tuning of crosslinking density and void spaces within the inverse opal hydrogel which will consequently affect response time. In this report, we present a fabrication of inverse opal hydrogel pH sensor based on template photo-polymerization of pH-sensitive hydrogel with exceptionally rapid kinetics and long-term stability. Optimization of fabrication processes including photo-polymerization of hydrogel, and the response time upon repeated pH variation is rigorously investigated.

2. Materials and methods

2.1. Materials

Three different Polystyrene (PS) microspheres (PS-220, PS-240, PS-260) with diameters of 220, 240, and 260 nm were used for preparation of the colloidal crystal template structures. PS-220 was purchased from Alfa Aesar, and PS-240 and PS-260 were synthesized by emulsion polymerization following a published procedure [16]. Styrene monomer (≥99%, Aldrich) was used after purification through activated aluminum oxide (basic, Acros). Potassium persulfate (99.99%, Aldrich) (initiator) and sodium dodecyl sulfate (>99.8%, Aldrich) (surfactant) were used as received.

For the templated photo-polymerization of the pH-responsive hydrogel, 2-hydroxyethyl methacrylate (HEMA) (96%, Junsei), acrylic acid (AA) (99%, Junsei), and ethylene glycol dimethacrylate (EGDM) (98%, Aldrich) were used as monomers without further purification. Irgacure-651 (Ciba Specialty Chemicals) was used as the photoinitiator.

2.2. Syntheses of PS microspheres

Emulsion polymerization of PS-240 was performed following a published procedure [16]. Briefly, 5 mg of sodium dodecyl sulfate (SDS) and 50 mg potassium persulfate were mixed with 15 mL of deionized (DI) water in a 25-mL round bottomed flask and degassed by nitrogen bubbling. The flask containing the mixture was placed in a water bath at 70 °C, and further degassed for 30 min. 3 ml of styrene monomer was injected using syringe, and reaction was run with vigorous stirring for 4 h. The crude emulsion was filtered through a glass filter and kept in a semi-permeable Membrane (Cellu Sep T4, Membrane Filtration Products) which was soaked in 5 L of DI water for removal of unreacted monomer and surfactant. DI water was continuously replenished until resistivity reaches 12 MΩ. Finally, the ~10 wt% of PS emulsion was kept in a bottle, containing a small amount of ion exchange resin (AG501-X8, Bio-Rad) added for maintaining the purity of water. The procedure for emulsion polymerization of PS-260 was the same except 3 mg of SDS was used.

2.3. Fabrication of colloidal crystal template

Colloidal crystal templates were fabricated by modifying the flow cell method reported by Park et al. [17,18]. A standard microscope slide glass was cut to $25 \times 38\,mm^2$, and used as a bottom substrate. For a top substrate a hole (diameter = 3 mm) was made at the center of a slide glass using high speed mini bench drill (Seogwang T&M). All substrates were treated with Piranha solution (H_2SO_4:H_2O_2 = 3:1 by volume), and rinsed with DI-water several times. The top substrate was made hydrophobic by soaking it in 1 mM trichlorooctadecylsilane (TCI) dissolved in 2,2,4-trimethylpentane (Jusei) for 30 min. Then a glass tube (length = 30 mm, diameter = 5 mm) was bonded to a hole of top substrate using epoxy resin (Hardex). At this stage, the whole top surface was evenly coated with the same epoxy resin to have ~3 mm thickness. As a spacer, a square cut Mylar film (thickness: 25 μm, Cheil Industry) having an open space of $10 \times 15\,mm^2$ area at the center was pre-cleaned with ethanol, and the channels were made using razor blade for discharging water during the colloidal crystallization. A Mylar spacer was placed between the bottom and the top substrate, and tightly clipped using six metal clips. The emulsion of PS microsphere was diluted to 0.4 wt%, and ~0.5 mL aliquot was introduced through the glass tube on the top substrate which was subsequently pressurized by rubber bulb. The complete cell was placed in ultrasonicator (JAC Ultrasonic 2010, KODO) by 30°, and colloidal crystallization was performed for several days. The smaller microspheres required a longer crystallization period. Once the colloidal crystal was formed, the cell was air-dried, and subsequently annealed in a vacuum oven (LK-Lab) at 60 °C for 4 h [17,18].

2.4. Preparation of inverse opal hydrogel pH sensor

2.5 g 2-hydroxyethyl methacrylate (HEMA, Junsei), 35 mg Acrylic acid (AA, Junsei), 25 mg Ethylene glycol dimethacrylate (EGDM, Aldrich), 75 mg Irgacure-651 (Ciba specialty Chemicals) and, 0.625 g DI-water were mixed a vial, and ultra-sonicated for 10 min using a bath sonicator (SD-80H, Seong Dong). The polymerization mixture was infiltrated within the colloidal crystal template though the glass tube of a flow-cell, and air pressure was exerted to facilitate infiltration. After remaining liquid was removed, photo-polymerization was performed using a high intensity UV-lamp (SB-100P/F, Spectronics Corporation) through a neutral density filter (Edmund optics) or a home-made epoxy filter (Hardex) for 2 h. Upon completion of photo-polymerization, the top substrate and spacer were removed from the flow-cell, and the templated hydrogel was dipped in chloroform (Duksan pure chemicals) for 24 h to remove PS colloidal template. Subsequent rinsing with chloroform and dipping in acetonitrile (ACN, Duksan pure chemicals) produced an iridescence which reflects a successful polymerization of the inverse opal hydrogel structure. The hydrogel was finally soaked in pH 1.5 phosphate buffer solution via DI water. A typical procedure for the preparation of hydrogel sensor is illustrated in Fig. 1. The phosphate buffer solutions of various pH were prepared by mixing different volumes of 0.1 M KH_2PO_4 (aq.) (Duksan pure chemicals), 0.1 M HCl (aq.) (Samchun chemicals), 0.1 M NaOH (aq.) (Samchun chemicals). pH measurement of the hydrogel sensor was performed using a pH meter(SP-701, Suntex) at ambient temperature.

2.5. Characterizations

Structural characterizations of the colloidal crystal and the resultant inverse opal hydrogel were performed using Hitachi S-4700 field-emission scanning electron microscope (SEM). The inverse opal samples were dried in vacuum oven (LK-Lab) at ambient temperature overnight, and subsequently freeze-fractured using liquid N_2. The reflectance spectra from the colloidal crystals were obtained using a fiber optic UV–vis spectrometer (AvaSpec, Avantes) coupled with a reflected light microscope (L2003A,