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Visual multi-triggered sensor based on inverse opal hydrogel

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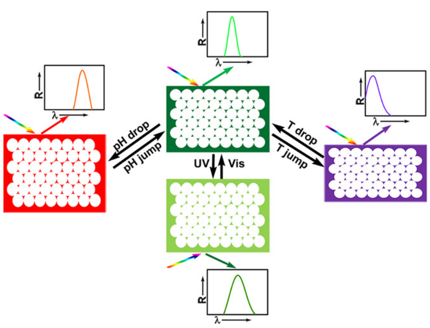
GRAPHICAL ABSTRACT

A novel visual multi-triggered sensor based on inverse opal hydrogel was prepared, which responses to pH, temperature and light, respectively.



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ABSTRACT

Smart hydrogels are regarded as novel sensors due to large reversible volume change in response to external stimuli. Here we prepared a novel visual multi-triggered sensor based on inverse opal hydrogel (IOH) that responses to pH, temperature and light, respectively. The hydrogel was composed of hydrophilic pH and temperature responsive poly(dimethylaminoethyl methacrylate) (PDMAEMA), and light responsive spiropyran-containing segment. When the pH decreased, the sensor changed its structural color from blue to orange-red, and the structural color was reversibly recovered by increasing pH. In addition, the color of sensor can be controlled to change from green to violet while applying a temperature field. Furthermore, the reflection peak of IOH exhibited obvious shifted behavior by UV/visible irradiation. Repeated condition changes revealed that the sensor has a long lifetime.

1. Introduction

Photonic crystals with periodic structure have attracted widespread attention because of inherently brilliant structural color through Bragg diffraction [1,2]. This provides a promising future in the field of optical communications, such as photonic crystal fiber [3] and all-photon integrated circuits [4]. Many studies have focused on responsive materials that undergo conformational transformations with changes in the external environment [5–8]. Thus, photonic crystals coupled with responsive materials are able to not only functionalize but also visualize by varying the structural color in respond to external stimuli, such as temperature [9,10], light [11,12], vapor [13,14], mechanical stress [15–18], chemical reagent [19,20] and biomolecules solvent [21–23], which realizes the conversion of environmental parameters into optical signals. In particular, hydrogels that have elastic polymer network are an appropriate candidate responsive material [24–26]. The responsive

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photonic crystals based on hydrogel generally contain two types, one is the polymerized crystalline colloidal array (PCCA) [27], and other is the inverse opal hydrogel (IOH) [28]. It is noteworthy that the IOH has a faster response speed and stronger mechanical stability than the opal structure due to its mesoporous structure that facilitates the circulation of the liquid to bind the stimulus. In order to create different functional sensors to suit specific environments, it is understandable in previous reports that changing the sensing moieties or fabrication routes is acceptable [29,30]. For instance, Shin et al. prepared a mechanically robust and fast responsive IOH sensor for pH with a responsive time of less than 10 s upon changing pH [31]. Zhao et al. synthesized IOH consisting of poly-2-hydroxyethyl methacrylate, of which reflection spectra can be tuned over the entire visible-light range by immersing them into different chemical solutions [19]. Couturier et al. designed a new IOH biosensor for detection of (bio)macromolecules based on combination of oligo(ethylene glycol) macromonomers with comonomer units with various recognitions [32]. Until now, except the single response IOH sensors, dual responsive IOH sensors have attracted great interest. For example, Ueno et al. presented an IOH that exhibits various, switchable colors depending on temperature and electric field change [33]. Matsubara et al. chose two different functional monomers, containing temperature sensitive monomer N-isopropylacrylamide (NIPA) and light sensitive 4-acryloylaminoazobenzene (AAB), to obtain the dual responsive IOH [34]. However, it is necessary that sensors are able to respond to multiple stimuli for complicated environment, which will benefit the applications of such sensors in the future.

In this work, we prepared a novel triple responsive sensor based on IOH for pH, temperature and light responses, respectively. The IOH sensor was fabricated by thermo-polymerization of hydrogel monomers, which mainly contains dimethylaminoethyl methacrylate (DMAEMA) and spiropyran-mathacrylate (SPMA) within the interstitial space of silica colloidal crystal template. The fabrication and operating mechanism of the triple responsive sensor are schematically represented in Fig. 1. Here we investigated responsive behavior of the IOH and sensing mechanism in different condition (*i.e.*, pH, temperature, UV light). In addition, the relationship between cross-linker contents and the swelling ratio of gel network was detailed analyzed. The repeated condition changes revealed that the sensor has a long lifetime. Therefore, this triple responsive IOH can be valuable in a wide range of applications such as environment monitor and sensing materials.

2. Experimental section

2.1. Materials

Anhydrous ethanol, methanol, ammonia and n-propyl alcohol were of reagent quality and purchased from Beijing Chemical Reagent Co. Ltd. Tetraethyl orthosilicate (TEOS, 99%, Energy) was distilled under reduced pressure before use to remove impurities. 2-(*N,N*-dimethylaminoethyl) methacrylate (DMAEMA, Energy, 99%) was dried over CaH_2 and distilled under reduced pressure. Spiropyran-mathacrylate (SPMA) monomer containing a single ester linkage was synthesized as described previously [35]. The initiator 2,2′-azobis(isobutyronitrile) (AIBN, 98%, Energy) was purified by recrystallization in ethanol. The cross-linker N,N′-methylenebisacrylamide (BIS, 100%, Energy) was used as received. All ITO glasses were cut to 3 cm × 2 cm, then treated with piranha solution to enhance hydrophilicity, and finally repeatedly rinsed with ethanol and deionized water for three times, respectively.

2.2. Synthesis of colloidal SiO_2 microspheres

The monodisperse SiO_2 microspheres were synthesized by the Stöber sol-gel method [36]. 4 mL of ammonia and 50 mL of mixtures of anhydrous methanol-*n*-propyl in a ratio of 1:3 were added in flask and stirred for 20 min at 30 °C. Then 4 mL of TEOS was dropwise added by using a constant pressure funnel while stirring. After 12 h of reaction, the silica spheres with diameter of 270 nm were obtained. Then the silica particles were purified by centrifugation and rinsing with anhydrous ethanol. The obtained silica particles were redispersed in ethanol with a concentration of 3 wt%.

2.3. Preparation of opal template

The colloid crystals of SiO_2 microspheres were fabricated by a vertical deposition method [37]. A clean ITO glass sheet was vertically immersed into the synthesized SiO_2 microspheres suspension. Then, the SiO_2 suspension was located in a vacuum drying oven at constant temperature of 42 °C under certain negative pressure. After ethanol in the colloidal suspension was completely evaporated, a solid structure of well-ordered SiO_2 opal template on glass slide was obtained.

2.4. Preparation of multiple-responsive inverse opal hydrogel sensor

A main procedure for the preparation of IOH sensor is schematically illustrated in Fig. 1a. The IOH film was obtained by a capillary attraction-induced method as follows [38]. First, the mixtures containing 1.5 g of temperature and pH responsive monomer DMAEMA, 20 mg of photo responsive monomer SPMA, 15 mg of cross-linker BIS, and 15 mg of initiator AIBN were dissolved in 0.2 mL of ethanol, and ultra-sonicated for 15 min using a bath sonicator. Second, the slide of opal template was covered with a poly (methyl methacrylate) (PMMA) slide with same size. The precursor solution was then injected into the cell *via* capillary forces and allowed to permeate for *ca.* 15 min until the template became transparent. Then, the precursor solution in cell was polymerized at 60 °C for 24 h. Third, the acquired samples were immersed in 5 wt% of HF aqueous solution at room temperature for 1 day to etch off the SiO_2 microspheres. Fourth, after completion of the etching process, the inverse opal-containing PMMA slide was separated from the glass slide. The sample was repeatedly rinsed with distilled water to remove residual HF and other impurities, and then was immersed in distilled water for 2 days until reaching a swelling equilibrium for characterizing the responsive behaviors of IOH sensor. The synthetic product is determined by the FT-IR spectra of DMAEMA, SPMA and poly(DMAEMA-co-SPMA) (see Supplementary data). The phosphate buffer solutions with various pH values were acquired by adjusting contents of 0.1 M HCl, 0.1 M NaOH. The pH value was measured by pH meter at 30 °C.

2.5. Characterization

The SiO_2 opal and IOH were coated with gold by a sputter coater (EM SCD005, LEICA, Germany), and then their surface morphologies were observed by using scanning electron microscope (SEM, SUPRATM 55, ZEISS, Germany). Reflection spectra of SiO_2 opal and IOH were measured by a fiber optic spectrometer (EX, NOVA, U.S.A.). The corresponding color changes were visualized by a digital camera (DS-Ri1, Nikon, Japan) under a daylight lamp. For the pH-response test, the IOH was soaked in the corresponding pH phosphate buffer solution at 30 °C for 2 h to reach a stabilization. Then the excess water on the surface of IOH was removed by using filter paper. The IOH was placed on heating stage with a temperature of 30 °C for test. For the thermo-response test, the sample was soaked in the phosphate buffer solution (pH = 7) with corresponding temperature adjusted by the water bath for 2 h. Then the excess water was removed by using filter paper. The IOH was placed on heating stage with corresponding temperature for test. The swelling measurement was implemented by monitoring the length of the cylindrical gel in different external conditions.