Dually responsive one dimensional photonic crystals with reversible color changes

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ABSTRACT: We developed a smart and reproducible fabrication of pH/temperature dually responsive sensor by taking advantage of one dimensional photonic crystals (1DPCs). TiO_2 /P(AA-bis-NiPAAm) 1DPCs were fabricated by spin-coating TiO_2 and copolymers P(AA-bis-NiPAAm) onto silicon wafers. When using the 1DPCs dually responsive polymer films as pH/temperature sensor, both refraction wavelength and peak refraction intensity values were derived, and the reproducible change could be observed by the naked eye through a change in color.

KEYWORDS: 1DPCs, dually responsive, P(NiPAAm-bis-AA), TiO₂

1. Introduction

Photonic crystal hydrogel sensor exhibits “structural color” due to the selective diffraction of light from periodic structures of the hydrogel.[1-5] Binding of analyte to the functional group of the hydrogel causes osmotic pressure increase in the hydrogel, and the following volume change of the hydrogel sensor driven by water influx to compensate the osmotic pressure directly induces a change in structural color.[6-12] The reversible sensing behavior has potential applications in chemical and biological sensors.

Due to this reversible color tunability by external stimuli, the hydrogel sensor can be categorized as a smart photonic crystal.[13] Two of the most attractive features of the photonic crystal hydrogel sensors are easy recognition of stimuli by naked eye without necessity of complex detection systems, and reusability of the sensor as long as the stimuli binding to the hydrogel is a reversible process.[14] As a typical example, acrylic monomer containing the sensing moiety is copolymerized with hydrogel monomer such as 2-hydroxyethyl methacrylate (HEMA) and a suitable cross-linker.[15, 16] Various stimuli-responsive hydrogel sensors can be fabricated by changing the monomers.[17-19] Gu and coworkers demonstrated tunable photonic crystals beads composed of ethoxylated trimethylolpropane triacrylate (ETPTA) and polyethylene glycol (PEG) for multifunctional biomedical applications.[20] Ever since the pioneering work reported by some researchers, there have been lots of investigations on photonic crystal hydrogel sensors for such as pH[16, 21], humidity,[22] temperature,[23] metal ions,[24, 25] glucose,[26] and so on.[27]

By introducing more than one sensing moieties into the hydrogel system, multi-response hydrogel sensors can be produced. Takeoka and coworkers reported on a dual tunable sensor for thermo and pH by copolymerizing methacrylic acid (MAA) and N-isopropylacrylamide (NiPAAm).[28]

Zhang and coworkers demonstrated a glucose–temperature dual sensor.[29] Takeoka and coworkers also fabricated photochromic hydrogel sensor which responds simultaneously to the UV-light and temperature by copolymerizing NiPAAm and azobenzene-containing acrylic monomer where azobenzene unit in the hydrogel induced volume change through the photo isomerization process.[30] Among this research works, NiPAAm is a well-known functional hydrogel which exhibits a thermo responsive volume transition by lower critical solution temperature (LCST) behavior at about 32 °C. Below LCST, NiPAAm swells by being compatible with water while it collapses over LCST due to the hydrophobic transition.

Sensing materials for temperature, pH, redox-active compounds, ionic species, glucose, solvents, light, magnetic fields, and electric fields have been prepared in 3D photonic crystals dual-responsive systems.[31] When turn the attention to 1DPC, it provides easy fabrication process, ordered stack structure with controllable composite layer thickness and controllable responsiveness.[32, 33] Incorporation of functional nano-materials within 1DPCs template is regarded as a clever idea toward many useful applications such as colorimetric sensors,[34, 35] solar cell,[36] and high index photonic band gap materials.[37, 38] Among those, responsive 1DPCs with stimuli-response hydrogel have drawn a growing interest over the last decade due to its potential toward various “smart” sensor applications.[32, 39-44] However, there have been few reports on dual-responsive hydrogel 1DPCs which can independently and extensively response to two stimulus.

In this study, we present a smart and reproducible fabrication of pH/temperature dually responsive sensor with rapid responses by copolymerizing AA and NiPAAm within the $\text{TiO}_2/\text{P}(\text{AA-bis-NiPAAm})$ 1DPCs structure which have ordered stack structure, controllable

composite layer thickness and controllable responsiveness. (see Figure 1). In addition to the responsiveness investigation, the reversibility of the sensor responses upon consecutive pH and temperature variations are also demonstrated. These features make 1DPCs ideal for sensing applications.

2. Materials and methods

2.1. Materials

As monomers for hydrogel, acrylic acid (AA, Sigma Aldrich), N-isopropylacrylamide (NiPAAm, Sigma Aldrich) were used. N, N'-methylene-bis-acrylamide (BIS, Sigma Aldrich) and ammonium persulfate (APS; Sigma Aldrich) was used as crosslinker, and thermal initiator respectively. 9.72 mmol NIPAm, 0.48 mmol of AA, 0.81 mmol of BIS, 0.29 mmol of APS, and 34.7 mmol of DI water were mixed. Synthesis of the TiO₂ Sol: Tetrabutyl titanate (20 g) was dissolved in 20 g of ethyl alcohol with stirring for 1 h. Acetic acid (2.12 g), hydrochloric acid (4.06 g), and ethanol (7 g) were then mixed homogeneously followed by adding dropwise into the above solution and stirred for another 3 h. The obtained yellow transparent solution was allowed to undergo hydrolysis reaction at room temperature overnight. The phosphate buffer solutions of various pH were prepared by mixing 0.1 M aq. KH₂PO₄ with HCl or NaOH.

2.2. Fabrication of dually responsive hydrogel 1DPCs

The 1DPCs were fabricated by spin-coating the TiO₂ sol and PNiPAAm-bis-AA alternately; both the TiO₂ sol and the polymer precursor were spin-coated at 3000 rpm for 30s onto a silicon wafer. In order to get different film thicknesses, compositions can be diluted into different concentrations or spin-coated in different rotate speeds. The TiO₂ layer was baked at 60 °C for 10 min and the polymer layer was baked at 135 °C for 10 min. The first layer was TiO₂ layer and the last layer

was polymer layer in all our experiments. The total number of the layers is 6, which means there is 3 bilayers structure.

2.3 Measurements of sensing responses

Scanning electron microscopy (SEM) images were obtained from a field emission scanning electron microscope (FE-SEM, HitachiS-3000N, Japan). In situ reflectance spectra were collected by a fiber optic spectrophotometer (Ocean Optics, Inc., HR 2000 256 UV-Vis-NIR). Angle dependence intensity spectra were obtained by Spectroscopic Ellipsometry (Semilab GES5E). Color photos were taken on a digital camera (Canon5D Mark II, Japan). Measurement of sensor response carried out by collecting a series of reflectance during pH or temperature changes. For temperature/pH dependent measurement, a sample was placed in a home-made vessel.

3. Results and discussion

The smart and reproducible fabrication of pH/temperature dually responsive 1DPCs were achieved through alternating TiO_2 and P(NiPAAm-bis-AA) by spin-coating. TiO_2 layer is chosen because of its high refractive index compared with polymer layer and stable structure in sensing process. Furthermore, it can form uniform film easily. The effective refractive indexes of the P(NiPAAm-bis-AA) and TiO_2 layers were determined by spectroscopic ellipsometry to be 1.585 and 1.831 respectively.

3.1 Optical properties of 1DPCs

Tuning of optical properties of 1DPCs can be achieved by increasing the number of layers, which is shown in Figure 2. An intense and wide Bragg peak (with peak position at 575 nm) is observed, which is a direct consequence of the large refractive index contrast between the TiO_2 layer and polymer layer. The photonic band width becomes narrower and the intensity of the peak grows

with increasing numbers of layers, which are in good agreement with previous theory of the thickness dependence of the optical response of photonic crystal slabs, Fig. 2(a).

A change of the layer thickness also influences the optical properties of 1DPCs. Increasing the layer thickness, the position of band gap will make a red shift due to Bragg-Snell's law, see in supporting information. [45] According to the significant refractive indices difference between two components, the obvious photonic stopband and structural color can be easily obtained in several bilayers. As shown in the reflective spectra (Figure 2b), fixing the thickness of TiO₂ layer at a proper thickness, while changing the thickness of polymer layer increasingly, the Bragg peak positions are at 461 nm, 520 nm, 571 nm and 626 nm respectively, which agrees with the experiment results. We can see that the Bragg peak positions increase direct proportionably when increasing the thickness of one layer while keeping the other layer constant. The Bragg peak can be manipulated in the full visible range from blue to red by choosing proper periods. The film is very uniform over a large area, see in Fig. 2(c, d). In our experiments, color uniformity can be achieved over an area of 15 mm×15 mm at least. The 1DPCs can keep its color invariable for a long time, which indicates that the prepared materials and microstructures have perfect stability.

3.2 Temperature and pH dually response sensing

This dual-responsive 1DPC is composed of NiPAAm, acrylic acid (AA), and N, N'-methylene-bis-acrylamide (BIS). An extensively studied water soluble thermo responsive polymer is PNiPAAm, which undergoes a phase transition at about 32 °C, expelling the majority of its solvating water in the process. The unique properties can be used to synthesize a variety of hydrogels with varying chemical and physical properties. The addition of co-monomers to the hydrogels can impact their responsivity and can have a strong impact on the photonic structure.

One common co-monomer is acrylic acid (AA). As a monomer, AA has an acid dissociation constant (pK_a) of about 4.25 at 25 °C. Moreover, the pK_a values of AA copolymerized in polymers are larger than 4.25, as a result of electrostatic interaction between neighboring AA monomers.[21]

In Fig. 3, typical sensing responses upon temperature or pH stimuli are shown. The size of the 1DPC in the photographs is 15 mm $\times$ 15 mm. The reflectance spectrum of a 1DPC usually includes the reflection maxima at visible wavelength range which stands for the structural color of the sensor varying with external stimuli. Fig. 3(a) shows the reflectance spectra measured at six different temperatures under fixed pH of 4.0. At a fixed pH, the temperature variation from 25 °C to 50 °C induced the band gap position changes from 600 nm to 505 nm as well as the colors of the 1DPCs change from red to green at different temperatures which are shown as photographs on bottom in Fig. 3(b).

Figure 4 shows the pH-dependent reflectance spectra at seven different pH buffers under the fixed temperature of 35 °C. According to Figure 4, when a PNiPAAm-bis-AA is at about pH 7.0 exhibits dramatic swelling power, resulting from both electrostatic repulsion between the charges on the polymer chains and osmotic pressure of the counterions.[46] Likewise, pH variation from 8.0 to 2.0 induced the band gap position changes from 575 nm to 510 nm, Fig. 4(a), at a fixed temperature of 35 °C induced the color change of the sensor from yellow to blue-green, Fig. 4(b)

The sensor responses upon pH and temperature stimuli can also be demonstrated by showing the changes of with respect to the stimuli conditions. Fig. 5a shows max reflection wavelength changes upon temperature variation measured at seven different pH buffers. It is worth noting that there are significant jumps of max reflection wavelength along with temperature curves between

the pH 6.0 and 7.0 since pKa of AA within the hydrogel where the pH sensitivity is maximized.[47]

Since the 1DPCs sensors used in the current study well stacked on the silicon wafer substrate, we assumed that the swelling occurs only along the vertical direction to the substrate surface which changes the polymer layers' thickness. From the series of reflectance spectra obtained during both stimuli, time-dependent variations of reflection peak value were plotted during the initial stages of swelling as shown in Fig. 5b. After the pH driven transformation begins, the peak reflectance value gradually decreased as the refractive indices differences between water and the hydrogel became smaller. As the water infiltrate into the 1DPC structure, more swollen hydrogel generally possesses a lower refractive index than the shrunken state due to inclusion of water. The peak value of reflection get a decrease immediately. For T-variation case, however, the intensity of the peak sharply get a rise up within 20 s after which increasing reflectance was observed just opposite to the pH response. The initial rise and the following recovery of the reflection peak intensity can partly explain an exceptionally rapid response of the T-drop experiment. When T-variation is applied, the 1DPC film make a rapid color change which can be observed by naked eyes.

To confirm the performance of the PNiPAAm-bis-AA 1DPCs in practical applications, several circles of temperature and pH variation were tested. The reflectance spectra were recorded, and their peak wavelength values were collected for further analysis. The results were shown in Fig. 6. When fix the pH buffer at 4.0, Fig. 6a shows the reversible change in max of PNiPAAm-bis-AA 1DPC as temperature varies from 25°C to 50 °C. It can be seen that the PCs swell and deswell completely reversibly under different temperature. When fix the temperature at 35 °C, Fig. 6b shows the reversible change in max of PNiPAAm-bis-AA 1DPC as pH varies from 2.0 to 8.0. This

fact further indicates that PNiPAAm-bis-AA chains are firmly embodied on the silicon wafer, and the 1DPC has an excellent durability. Considering that free radicals can be unpredictably reactive in condensed phases, some covalent cross-linking may happen. This may be the reason that the introduced PAA cannot be washed out. These two oscillation results show excellent reversibility for 10 cycles, respectively. With its responsiveness and durability, this novel modified 1DPC can be potentially used in fabricating chemical and biochemical sensors.

Conclusion

In summary, by combining with dually-responsive copolymer and 1DPC fabrication method, we have successfully introduced a pH/temperature dually responsive P(AA-bis-NiPAAm)/TiO₂ 1DPC affording a new type of stimuli-responsive optical material with quick response time. When using the 1DPCs dually responsive polymer films as pH/temperature sensor, both refraction wavelength and peak refraction intensity values were derived, and the reproducible change could be observed by the naked eye through a change in color. Furthermore, it could contribute to a multitude of 1DPCs, implying that it could find applications in various areas, such as chemical sensors, and environmental monitoring.

Acknowledgements

The authors thank for the financial support of pre-research foundation for national science foundation and the Fundamental Research Funds for the Central Universities. This work is also supported by the fund for the analysis and testing of the large-scale apparatus from the Southeast University. Prof. Dr. Ge also thanks for the support from Prof. Gu Zhongze.

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Figure Captions

Figure 1. (a) Chemical structures of the NiPAAm, BIS and AA, (b) a schematic illustration of sensor fabrication, whereby polymer and TiO₂ are sequentially spin-coated to create a multilayer 1D photonic stack.

Figure 2. a) Reflection intensity of the 1DPCs with rising number of bilayers; b) Structural color variation and reflection spectrum of the 1DPCs with different layer thickness; (c) shows the cross-section SEM image of a 1DPC of 6 layers, from which we can see multilayered structure of the 1DPC. (d) shows that both of the two materials are 3 layers, and the average thicknesses of polymer layer and TiO_2 layer are 160 nm and 70 nm respectively.

Figure 3. (a) The reflectance spectra of 1DPCs exposed to different temperatures varies from 25 °C to 50 °C under pH = 4.0, temperature 32 °C was specifically noted. (b) Photographs of the as-prepared 1DPCs corresponding to different temperatures.

Figure 4. (a) The reflectance spectra of 1DPCs exposed to different pH varies from 8 to 2 under temperature = 35 °C. (b) Photographs of the as-prepared 1DPCs corresponding to different pH.

Figure 5. (a) Reflection maxima changes of a dual tunable 1DPC hydrogel sensor with respect to temperature variation measured at seven different pHs. (b) Plot of peak reflectance vs. time from the consecutive reflectance spectra obtained during pH change from 8 to 2 (red plots), and temperature from 25 °C to 50 °C (black plots).

a)

b)

Figure 6. (a) 10 times reversible changes of the stopband of the 1DPC with temperature changes from 25 °C to 50 °C under pH 4.0. (b) 10 times reversible changes of the stopband of the 1DPC with pH changes from 2 to 8 under temperature 35 °C.

A smart and reproducible fabrication of pH/temperature dually responsive sensor by taking advantage of 1DPCs