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Novel pH-sensitive photopolymer hydrogel and its holographic sensing response for solution characterization

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ABSTRACT

Optical sensor based on pH-sensitive hydrogel has important practical applications in medical diagnosis and bio-sensor areas. This report details the experimental and theoretical results from a novel photosensitive polymer hydrogel holographic sensor, which formed by thermal polymerization of 2-hydroxyethyl methacrylate, for the detection of pH in buffer. Volume grating recorded in the polymer hydrogel was employed in response to the performance of solution. Methacrylic acid with carboxyl groups was selected as the primary co-monomer to functionalize the matrix. Peak diffraction spectrum of holographic grating determined as a primary sensing parameter was characterized to reflect the change in pH. The extracted linear relation between peak wavelength and pH value provided a probability for the practical application of holographic sensor. To explore the sensing mechanism deeply, a theoretical model was used to describe the relevant holographic processes, including grating formation, dark diffusional enhancement, and final fringe swelling. Numerical result further showed all of the dynamic processes and internal sensing physical mechanism. These experimental and numerical results provided a significant foundation for the development of novel holographic sensor based on polymer hydrogel and improvement of its practical applicability.

1. Introduction

Recently, the interesting in holographic analytes sensitive medium for environmental monitory has been increasing [1–6]. Specially, holographic sensors formed by photopolymer as a novel optical sensing device have attracted much attention. Holographic sensor as a novel and effective strategy is a potential optical sensing platform in bio-sensing area due to its narrow diffraction spectrum, high visualization and stability, low cost of preparation and detection [7,8]. In previous reports, the diffraction grating has been formed by periodic arrangement of Ag nanoparticles with size reduction [9]. In addition, nanoparticle as a dopant was dispersed into the polymer material to enhance the relative performance [10–14]. This method has some disadvantages, including complex preparation method and expensive instrument. Construction of holographic sensor with simple fabrication, low cost, high stability still remains a great challenge.

Compared with previous holographic sensor formed by periodic arrangement of nanoparticles, the photopolymer can be considered as a significant candidate for next generation holographic sensor [15,16]. The photopolymer used for holographic data storage and relative optical elements has attracted much attention in recently years [17–20]. The evident characterization, such as high diffraction efficiency, low cost and self-process, reduces the entry barriers for clinic application of holographic optical elements [21–23]. The holographic volume grating can be formed by direct coherent light writing in the photopolymer. Nevertheless, there are some disadvantages which inhibited the application of photopolymer in holographic sensing area. One major disadvantage is the survival stability of volume grating in aqueous solution. The volume grating is water soluble in promising photopolymer, for example acrylamide system [24,25]. Despite replacing the components, the survival time in water and high relative humidity is very transient. Secondly, the inherent components in some photopolymers limit the selection of matrix and functional monomers [26].

In this paper, a novel photosensitive polymer hydrogel system was proposed for improving the applicability of holographic sensor in solution. The polymer with high survival ability in water was used to sense the solution characterization by copolymerizing

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the functional monomer. The pH sensitivity of novel holographic sensor was demonstrated experimentally. The sensing physical mechanism and corresponding theory were proposed to describe the grating formation and holographic sensing process, including photochemical process during grating formation, dark development and swelling dynamics during sensing process. The extracted relation between diffraction spectrum characteristics and pH was introduced into the model. The detailed calculated results were presented. These theory and experiments will accelerate the development of holographic sensor based on photosensitive polymer hydrogel.

2. Material and experimental setup

2.1. Material

In experiments, a photosensitive poly (2-hydroxyethyl methacrylate) (PHEMA) hydrogel system was developed to fabricate the holographic sensor. The preparation strategy of the hydrogel was thermally polymerization of components induced by thermal initiator. The primary monomer component was 2-hydroxyethyl methacrylate (HEMA). The thermal initiator was 2,2-azobis (2-methlpropionitrile) (AIBN), and the crosslinker was ethyleneglycol dimethacrylate (EGDMA). Phenanthrenequinone (PQ) molecules as photosensitizer was dispersed into the sample to induce photo-polymerization for recording volume grating. In order to sense the pH of phosphate buffer saline, meth-acrylic acid (MAA) monomer was dissolved into the mixture for functionalizing the hydrogel. MAA could reversibly binds H^+, and it is sensitive to the changes in pH of buffer. A simple and effective method was used to enhance the PQ's concentration and materials photosensitivity. Generally, only up to 0.7 wt% PQ molecules could dissolve into the 2-hydroxyethyl methacrylate (HEMA) at room temperature. The preparation procedure can be described as follows. Firstly HEMA was weighted into a weighting bottle. Then the other primary components, namely, PQ, AIBN, MAA, EGDMA, were dissolved into HEMA solution. Subsequently, the mixture of PQ, AIBN, MAA, EGDMA and HEMA was purified at 60 °C until it returned to a uniform solution. After this process, PQ molecules with concentration 1.0 wt% approximately were dissolved into the sample. The detailed components and their weight percentage were listed in Table 1. Subsequently, the purified mixture was injected into a mold and temperature was increased to 70 °C for initiating the chain polymerization. Finally, the mixture was placed for 48 h at constant temperature 60 °C. After releasing the mold, the sample was employed to fabricate the holographic sensor. The Schematic preparation procedure of sample was shown in Fig. 1(a).

2.2. Experimental setup

In our holographic sensor, a holographic volume grating was used as a sensing element. The schematic experimental setup was shown in Fig. 1(b). Fig. 1(c) shows a picture of sample. An asymmetric two-beam coupling geometry was used to record the slanted reflection grating. The recording light wavelength was operated at 532 nm, which can be used to write grating. A supper-continuum laser was incident into the medium in the opposite direction relative to the green light. The supper-continuum laser was purchased from Wuhan Yangtze Soton Laser Co. Ltd. A reflection grating with slanted angle 10 deg could separate the diffraction beam from the reflected beam to improve the accuracy of sensing measurement. The diffraction spectrums of volume grating were measured using Qwave fiber spectrometer, which was purchased from RGB Photonics Co. The optical spectrum resolution (FWHM) was 0.5 nm, provided by the manufacturer.

3. Theoretical description

3.1. Photochemical process and sensing mechanism

The photoattachment process in the materials is similar as the typical PQ-PMMA (phenanthrenequinone doped polymethyl methacrylate) photopolymer [27–30]. The latter is common material in the field of optical data storage and optical communications [31,32]. The photochemical process can be described as follows. Under illumination, the PQ molecules firstly absorb the photons to transform into its triplet excited state. Then the PQ molecules in excited state initiate the polymer matrix to form the corresponding free radicals. Finally, the PQ free radicals attach to the polymer matrix to form the steady photoproducts. In addition, a few photoattachment of PQ to HEMA residual monomer cannot be avoid. However this attachment not effects the grating formation. Actually, the grating formation is attributed to the structure change of PQ molecules, which induces a strong modification of refractive index [32]. The complex photochemical processes can be simplified as follows,

$$PQ \xrightarrow{h\nu} {}^3PQ, \tag{1}$$

$$^3PQ + HR \rightarrow HPQ^{\cdot} + R^{\cdot}, \tag{2}$$

$$R^{\cdot}_{n-1} + R \rightarrow R^{\cdot}_{n}, \tag{3}$$

$$HPQ^{\cdot} + R^{\cdot} \rightarrow RQPH, \tag{4}$$

where R represents the HEMA molecules ($n \geq 1$) and PHEMA polymer ($n > 1$). ^3PQ characterizes the PQ molecules in the triplet excited state. The schematic photo-polymerization process is described in Fig. 2. Actually, the photo-attachment separated from the thermally initiated polymerization has been considered as an effective method to enhance the grating strength [15,16]. The thermally initiated polymerization can enhance the matrix stability by thermal initiator AIBN. Simultaneously, the PQ photosensitizer isn't effected by the thermal polymerization. Subsequently, the photo-initiated process can bring the attachment of PQ to the polymer chain and the formation of refractive index grating.

Fig. 3 shows the holographic sensing mechanism, and the detailed is described as follows. The hydrogel sensing response depends on the co-monomer with functional side chains. For example, the ionization of carboxyl groups in MAA can enhance the osmotic pressure within the hydrogel and hence increase the

Table 1
Primary component for preparing the novel polymer hydrogel.

Components	Name	Abbreviation	Weight percentage
Monomer	2-Hydroxyethyl methacrylate	HEMA	95.0 wt%
Photosensitizer	9,10-Phenanthrenequinone	PQ	0.1 wt%
Thermal initiator	2,2′-Azobis(2-methylpropionitrile)	AIBN	0.5 wt%
Cross-linker	Ethyleneglycol dimethacrylate	EGDMA	0.6 wt%
Functional co-monomer	Meth-acrylic acid	MAA	3.8 wt%