



Full-color mechanical sensor based on elastic nanocomposite hydrogels encapsulated three-dimensional colloidal arrays

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ABSTRACT

A label free and easy-to-prepare optical sensor with high mechanical strength for the fast and visible response to tension and pH variables was reported. An elastic nanocomposite hydrogel was successfully fabricated by in situ free-radical co-polymerization of *N,N*-dimethylacrylamide (DMAA), acrylic acid (AA) and aluminum oxide nanoparticles (Al_2O_3 NPs). DMAA and AA could form effective cross-linkage with Al_2O_3 NPs via hydrogen binding, electrostatic interaction and bidentate bridging. By encapsulating poly-methyl methacrylate (PMMA) colloidal arrays into the hydrogels, the optical nanocomposite hydrogels (ONHs) can be easily obtained. This three-dimensionally ordered array exhibits a stop band, and the optical hydrogels can tune the bright color from blue to cyan, green, yellow green, yellow, orange and then finally red by mechanical stimulation of uniaxial tension within 50% strain following Bragg's law. The mechanical and optical properties can be adjusted via changing the fraction of AA and polymerization time. Meanwhile, the mechanical and optical responses were reversible for more than 10 times without deterioration. Besides, this material has rapid response to the changing of pH and the full-color change was observed. Owing to the high biocompatibility of nanocomposite hydrogel (NC gel) system and the excellent mechanical strength and water-stability of these ONHs, this optical sensor has high potential to be applied in biomedical field as tension or pH sensor for the intraocular pressure measurement and tonometry and blood gas analysis.

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1. Introduction

Photonic crystals (PhCs) with three dimensional structures are periodic lattices which can be assembled from the spherical colloidal particles [1–4]. These regular repeating structures have a stop band and satisfy the Bragg's law of diffraction, which is able to cover the entire wavelength range of visible spectrum and produce color [5,6]. After combined with hydrogels, the color switching can be simulated by various external chemical or physical stimuli, such as pH [7,8], ion strength [9,10], electrical [11,12], magnetic [13,14], thermal [15–18] or mechanical stimuli [19–21]. The volume change of the hydrogels caused by the external stimuli could lead to the diffraction wavelength shifts of PhC with color changes. Thus, considerable attentions have been drawn to the application of the PhC hydrogels as the responsive sensors due to their unique optical properties [22,23]. Furthermore, the hydrogels have

three-dimensional highly hydrated elastic polymeric network and fluid-filled inter-space of the network, and it's similar to the structure of living organism composed of polysaccharide network and protein [24]. Thus in the field of bio-sensing, the outstanding biocompatibility and hydrophilicity of the hydrogels provide them a high potential as implantable clinic sensors [25–29]. However, the practical applications are severely limited by their brittle mechanical behaviors and the high swelling ratio of the conventional organic polymeric hydrogels (OPHs) which are chemically cross linked [30].

Consisting of specific organic polymers and an inorganic water-soluble nanomaterial that acts as the multifunctional cross-linker [31–33], various of nanoparticles including carbon nanoparticles, metal/metal oxide nanoparticles and inorganic nanoparticles are applied to fabricate the nanocomposite hydrogels (NC gels). By the aid of the unique organic-inorganic network structure, the NC gels can overcome most of the disadvantages of OPHs and provide various types of novel properties [34,35], like the high mechanical properties [36,37] and self-healing ability [38,39]. By employing the elastic soft materials, the color tuning of the gel is based on

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the mechanical deformation instead of the swelling-shrinkage volume change [40], and ensures the time-dependent response. This unique mechanical behavior of the elastic hydrogel results from viscoelasticity and poroelasticity [41]. Thus, the color switching could instantly respond to the deformation and the NC gels recovered by the strength without any delay.

Herein, we proposed a new type of a novel elastic optical nanocomposite hydrogel (ONH) by in situ free-radical copolymerization of *N,N*-dimethylacrylamide (DMAA) and acrylic acid (AA) as monomers. The outstanding mechanical properties can be achieved by employing aluminum oxide nanoparticles (Al_2O_3 NPs) in solution as the multifunctional cross-linking agent. Furthermore, the ONHs are highly transparent, soft and have good water-stability. The full-color tunability and instantaneously color switching with a slight volume change of ONH might provide it a high potential application to be used as an implantable clinical sensing material.

2. Methods

2.1. Materials

Methyl methacrylate (MMA, 99%) was purchased from Bodi Chemical. Acrylic acid (AA, 99%) and aluminum oxide (neutral) were purchased from Sinopharm Chemical Reagent Co. Ltd. 2-hydroxy-4-(2-hydroxyethoxy)-2-methylpropophenone (Irgacure 2959, 98%) was purchased from Energy Chemical. *N,N*-Dimethylacrylamide (DMAA, 99%) was purchased from Kohjin Co. Ltd. Potassium persulfate (KPS) was purchased from Xilong Chemical Co. Ltd. Colloidal aluminum oxide nanoparticles (Al_2O_3 NPs, size = 20–40 nm in diameter) were purchased from Suzhou Nadi Microelectronics Co. Ltd. Beijing Chemical Plant provided the sulfuric acid (H_2SO_4 , 98%) and hydrogen peroxide (H_2O_2 , 30% water solution). Potassium dihydrogen phosphate (KDP) and potassium hydroxide (KOH) were purchased from Beijing Chemical Plants and Feng Chuan Chemical Reagent Science and Technology Ltd, respectively. All the chemicals were of analytical grade. AA and DMAA were purified by filtering through aluminum oxide, respectively, while the other chemicals were used as received without further purification. The deionized water used in all experiments was produced by Milli-Q Advantage.

The acrylic sheets, the centrifuge tubes, glass tubes and slides ($24 \times 24 \times 0.15$ mm) were provided by the Weiss Experiment Product Co. Ltd, China. The glass slides were cleaned and made hydrophilic by immersing them into a $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (7/3, v/v) solution for 12 h and then rinsing with water.

2.2. Fabrication of PMMA array

The monodispersed polymethyl methacrylate (PMMA) colloidal particles were prepared by using methods similar to those of Wang et al. [42]. MMA (6 mL) was mixed with 140 mL water in a four neck flask (250 mL). The mixture was deoxygenated by bubbling with nitrogen at 75 °C. The polymerization was initiated by addition of 5 mL KPS (0.3 g) water solution. The resulting mixture was stirred at 80 °C with 3000 rpm for 45 min. The resulting PMMA particles were centrifuged at 6000 rpm for 5 min and washed with deionized water. The particles were then washed three times with 15 mL deionized water for 40 min each with 3 min of sonication. The PMMA particles were dispersed in deionized water (0.2 wt%) and then stored in square glass containers in which the glass slides were inserted vertically. The PMMA dispersion was evaporated at 30 °C while exposed to a relative humidity of 50%. After completely evaporation of water, the PMMA particles were self-assembled

on both sides of the glass slides and formed close-packed three-dimensional colloidal array via vertical deposition.

2.3. Preparation of hydrogels

Firstly, 5 g Al_2O_3 colloidal solution (6%, $W_{\text{Al}_2\text{O}_3}/W_{\text{water}}$) was added into 20 mL disposable scintillation vial, and then 1.1896 g DMAA and 0.2162 g AA were added into the vial under 200 rpm stirring for 20 min. When the solution was mixed evenly, the vial was wrapped by tinfoil and 0.015 g Irgacure 2959 was added. Subsequently, the mixture was bubbled with N_2 for 15 min under stirring and then a vacuum pump was used to repel O_2 out of the solution for another 20 min. Finally, the solution was injected between two acrylic sheets which were separated by a 1-mm-thick PVC curtain with one piece of PMMA array in the space. By illuminating the solution with a 365-nm UV light for 1 h, the free radical polymerization carried out to form a 0.85 mm thick 3D PhC AA-DMAA- Al_2O_3 nanocomposite hydrogel. The obtained hydrogels were washed with deionized water three times to remove the unreacted monomer and other impurities. The hydrogels were stored in the freezer at 4 °C before the measurements.

2.4. Measurements and characterizations

The morphologies of the resultant PMMA particles, colloidal arrays and 3D PhC AA-DMAA- Al_2O_3 nanocomposite hydrogels were characterized by a scanning electron microscope (SEM, Quanta TM 250, FEI) with a beam voltage of 5–20 kV. The diffraction spectra of the nanocomposite hydrogels were recorded at 45° using a fiber optic UV-vis spectrometer (Avaspec-2048TEC, Avantes) with an Avalight-DH-S-BAL light source and a FC-UV600-2-SR fiber optic reflection probe. The color changes of the films were recorded by a digital camera at a constant angle. The mechanical properties of hydrogels were obtained by a Tytron 250 electronic universal tester (Mechanical Testing & Simulation., US) at room temperature. One piece of platelike hydrogel sample ($24 \text{ mm} \times 18 \text{ mm} \times 0.85 \text{ mm}$) was clamped along with the length and width axes by the load cell with a 10 N load cell at a crosshead speed of 3 mm/min. Because the hydrogels could be deformed during the tensile tests, the initial cross-section area of hydrogels was used to calculate the strength and modulus by the stress-strain curves. The swelling properties were evaluated by immersing ONHs in deionized water. The pH sensing measurements were carried out by immersing the 10×4 mm pieces of hydrogels in 20 mM KDP buffer solution with pH value changing from 4 to 10. The colors were recorded by a digital camera after sweeping the water on hydrogel surfaces.

3. Results

3.1. Characterization of optical nanocomposite hydrogels

Scheme 1 shows the construction of the ONHs. The ONHs were synthesized by in situ free-radical polymerization in the presence of Al_2O_3 nanoparticles (Al_2O_3 NPs) in an aqueous system. Al_2O_3 NPs were used as cross linker. The co-monomers are able to form effective cross-linkage with Al_2O_3 NPs via hydrogen binding, electrostatic interaction and bidentate bridging [43], which are mainly attributed to interactions between the hydroxyl groups of Al_2O_3 NPs and the ester groups of the polymer chains. By immersing the ONHs into deionized water, the anisotropic swelling properties of ONHs can be evaluated (see Fig. S1 in the Supporting information). The swelling ratio of ONHs along the length axis (L/L_0) and width axis (W/W_0) reached stable (1.08) after 12 h immersing, whereas no obvious swelling was observed along with the thickness axis (h/h_0). Thus the swelling along the top surface (length and width

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