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Ultrafast mechano-responsive photonic hydrogel towards multicolor displays via the pressure sensation

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ABSTRACT

In this work, the magnetic assembly combined with fast photopolymerization is applied for the preparation of mechano-responsive photonic hydrogel. The as-prepared hydrogel exhibits switchable color with ultrafast speed ($\Delta\lambda/t = \sim 1.2$ nm/ms) across a broad wavelength range ($\Delta\lambda = \sim 250$ nm), which is attributed to fast changing of the interparticle distance d of one dimensional (1 D) Fe_3O_4 nanoparticle chains fixed inside the hydrogel matrix in response to compressive force stimulus. The pressure chromatic sensitivity is high ($\Delta\lambda/\sigma = 20$–$40$ nm kPa^{-1}) in touch region. With the aid of 3D printing technique, we innovatively demonstrate simultaneous multicolor displays on the hydrogel.

1. Introduction

Responsive photonic crystals (RPCs) [1], as dielectrically periodical structures which change its optical properties upon external stimulus, have aroused tremendous interests recently. A series of these materials responsive to stimuli such as gas [2], solvent [3], temperature [4], mechanical force [5] and electromagnetic field [6–8], have been designed for optical sensors. For many applications, such as fast responsive sensors, optical switches or movie displays, the video-rate fast color switching and broad color tuning range are essential. In this respect, the response of swelling/deswelling volume dependent RPC bulk samples can be slow, as the response speed will decrease with the sample size squared [9]. Mechano-responsive photonic crystal [10], based on straightforward physical deformation, offers an opportunity to develop fast dynamic sensors and actuators. So far, there is still rare research on dynamically responsive PCs. Ge et al. developed a SiO_2/ethylene glycol-poly(ethylene glycol) methacrylate gel, showing fast response in millisecond level [11]. In our previous work, we demonstrated a mechanochromic gel based on Fe_3O_4 nanoparticle chains, presenting reversible color variation within 720 ms [12]. Then Zhu et al. fabricated a hydrogel with reversible color change within 1 s [13]. Especially, the lamellar hydrogel reported recently by Gong et al. exhibited an ultrafast (0.1 ms) color switching under mechanical stimulus [14]. However, the response speed must be enhanced to meet high demands of dynamic sensing or time consuming fabrication processes are involved in most cases. Herein, we describe the synthesis of an ultrafast mechano-responsive photonic hydrogel via an efficient strategy of magnetic assembly combined with UV polymerization, and further initiatively apply the hydrogel for simultaneous multicolor pixel displays.

2. Experimental

2.1. Chemicals and materials

Ferrocene ($Fe(C_5H_5)_2$, $>98\%$), hydrogen peroxide (H_2O_2, 30%), acetone (C_3H_6O, $>99\%$), acrylamide (AM), N,N′-methylene-bis-acrylamide (MBA) and ethylene glycol (EG) were purchased from Aldrich. Photoinitiator 1173 was supplied by Chembridge International Corp. Uniform Fe_3O_4 particles with average diameter of ~ 100 nm (Fig. S1) were synthesized by a solvothermal process according to our previous report [12].

2.2. Fabrication of mechanochromic hydrogel

The photonic hydrogel films were prepared as illustrated in Fig. S2. In a typical process, 0.01 g Fe_3O_4 particles, 0.76 g AM and 0.0025 g MBA (0.33 wt% with respect to AM) were added into 1.2 g EG and mixed homogeneously. Subsequently, 0.01 g photoinitiator

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1173 was added and rapidly stirred for seconds at room temperature. After that, part of the mixture solution was dropped into the interlayer between a glass slide and a clear plastic slide (25 mm × 50 mm × 0.6 mm). Under a magnetic field of about 700 G, brilliant color showed up in the solution due to the 1D magnetic chains formed. Finally, polymerized gel can be obtained after being exposed to UV initiation for ~30 s. After fully swollen in water for ~30 min, photonic hydrogel films were obtained.

2.3. Measurements

The reflection spectra were all measured using Ocean Optics, USB 4000. The images and videos of the hydrogel were captured by Nikon camera D3100. The templates with convex patterns were designed by 3D printer FDM CREATBOT. The photonic chains inside the hydrogel were characterized by scanning electron microscopy (SEM) with a QUANTA200.

3. Results and discussion

Fig. 1a is a photograph of the gel film, which presents uniform green color in an area of 25 × 50 mm^2. After fully swollen in water for ~30 min, free-standing hydrogel film showing rust red is obtained (Fig. 1b), and the reflection peak red-shifts from 526 to 757 nm (Fig. 1c). A cross-sectional SEM image of the structural-colored hydrogel confirms the existence of 1D magnetic chains (Fig. 1d). An amplified SEM image (Fig. 1e) further clearly shows that particles in the chains are separated with an interparticle distance, which is necessary for Bragg Diffraction [15].

The key idea of this work is the ultrafast mechanochromic color switching speed, which is confirmed by the performance of the hydrogel under cyclic compression-relaxations operated manually at almost the highest frequency. Movie S1 shows dynamic colors of the hydrogel evolved from red violet to cyan and then recovery in response to compression-relaxation, and the color change synchronously follows the ultrafast mechanical operation without any hysteresis. More interestingly, rainbow colors can be observed under gradient compressive stress. To quantitatively analyze the switching speed, consecutive images over 1 s are extracted from video footages. Fig. 2a indicates that a color switching cycle can be repeated for two times within 1 s. The time from red violet to cyan is ~200 ms, and the wavelength shift is $\Delta\lambda_{max}$ = ~240 nm (Movie S2). As a result, the switching speed ($\Delta\lambda$/t) is ca. 1.2 nm/ms. This represents the highest response speed for mechanochromic PCs, except for the lamellar hydrogel [14]. Meanwhile, we have monitored the spectra in continuous tens of cycles, although only 10 of them are shown here in Fig. 2b. 3D surface map show that the switching of wavelength is highly repeatable and the reflectivity only slightly fluctuates. The mechanism for mechanochromic response is illustrated in Fig. 2c. 1D magnetic chains in the hydrogel with an interparticle distance d give rise to red color shown on the hydrogel surface; upon a compressive force, the 1D chains are compressed, and thus d decreases to be d - Δd, which results in blue-shift color. Taken together, the mechano-response presented here is ultrafast and dynamically switchable with no hysteresis and decay in optical properties.

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We further analyze the pressure sensitivity of the hydrogel, especially in touch pressure region [16]. Fig. 3a–b show photos of the hydrogel under different pressures. The original hydrogel takes on tawny color at 757 nm. When a pressure from 0.82 to 11.7 kPa is exerted on the hydrogel in turn, the color gradually shift to reddish violet, red, yellow, green and cyan, and the wavelength finally blue shifts to 503 nm at cyan. Fig. 3c shows the pressure-dependent reflection wavelength, i.e., the wavelength (λ) decreases along with the increase of pressure (σ). Under a gradient pressure, the hydrogel

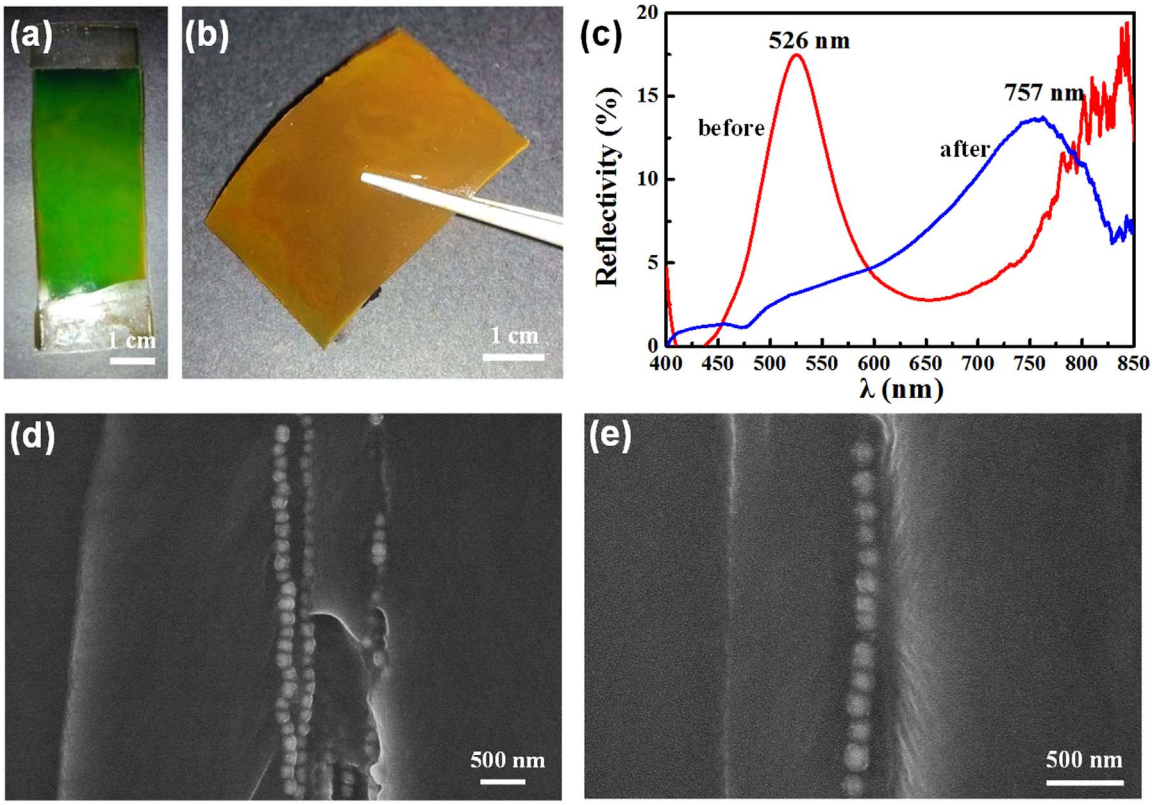

Fig. 1. Photographs of photonic hydrogel (a) before and (b) after swelling in water. (c) Reflection spectra of hydrogel before and after swelling. (d, e) SEM images of cross-sections of the hydrogel. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)