Photo-Patterning of Smart Light-Modulation Gel

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ABSTRACT: A novel method for fabricating desired patterns of smart light-modulation gels, which consist of thermoresponsive *N*-isopropylacrylamide (NIPAM) gel particles containing pigment, was developed. The patterns were fabricated by photo-patterning of dispersion of colored NIPAM gel particles in photosensitive poly(vinylalcohol)-styrylpyridinium solution. The pattern showed drastic color changes in response to the surrounding temperature changes. By repeated cycles of the patterning method, several independent patterns that contained different color particles were fabricated. In addition, a thermosensor array was also fabricated, which was constructed with independent patterns containing colored NIPAM gel having different color-changing temperatures. The patterning method studied here is considered to have strong potential to extend the application field of the smart light-modulation gels. J Appl Polym Sci 102: 5351–5357, 2006

Key words: stimuli responsive; hydrogel; photo-patterning; light-modulation; smart materials; biomimetic

INTRODUCTION

Stimuli responsive gels have attracted much attention as biomimetic materials, in such applications as artificial muscles and actuators, because these gels are soft, wet materials, similar to the tissues of a living organism, and change their volume and physical properties drastically in response to various external stimuli.[1–10] Our group has focused on the function of these gels as artificial muscles. We have recently developed, what we call, a smart light-modulation gel (hereafter referred to as LM gel), which imitates the function of pigment cells existing in the skin of cephalopods such as squid and octopi. The LM gel is composed of stimuli responsive gel particles containing high concentrations of colorant. According to the volume change of the colored gel particles, the light-absorption area covered by the gel alters; thus, the dispersion of the LM gel particles demonstrates excellent color-changing properties.[11] We have been investigating the light-modulation properties of LM gel particle dispersions applied over large areas and confirmed that LM gel has strong potential for various optical devices. If the LM gels can be arranged and fixed on a substrate in a specific pattern, the application area of the light-modulation gel will expand to optical devices, such as color filters for display devices and sensor arrays themselves. Here, we report a simple approach to make desired patterns with LM gel on a substrate utilizing a direct photo-patterning technique. By this method, LM gels with different colors and/or responding to different stimuli can be easily fixed into specific patterns. We also describe the fabrication of a thermosensor array utilizing LM gels of different color-change temperatures.

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EXPERIMENTAL

Materials

The poly(vinyl alcohol)-styrylpyridinium (PVA-SbQ) solution (SPP-S-13, degree of polymerization, 2300) was a gift from Toyo Gosei. Sodium dodecyl sulfate (SDS) was purchased from Wako Pure Chemical Industries. As colorants, we used self-dispersed pigments (Dai Nippon Ink; black pigment: MC black 082-E; blue pigment: MC blue 182-E; average particle diameters black: 85 nm, blue: 104 nm). *N*-Isopropylacrylamide gel particles containing 20 wt % of pigment was prepared by an inverse phase-suspension polymerization process. The details of the synthetic method have been reported elsewhere.[12] A UV-curable resin (Nihon Kayaku; KAYARAD R-381I) was used as a sealant of the edge of light modulators and a separator among patterns on the same substrate.

General procedure of the photo-patterning method

Aqueous NIPAM gel dispersion (2.0 g, gel solid content: 2.3 wt %), aqueous PVA-SbQ solution (2.0 g, 5.0 wt %), and sodium dodecylsulfate (12 mg) were mixed and stirred vigorously to disperse the NIPAM gel particles homogeneously. The resulting viscous dispersion was coated on a glass plate (100 × 100 × 0.9 mm^3), and laminated with another glass plate covered with a photomask. Monodispersed polystyrene particles (110 μm in diameter) were used to maintain the space between the glass plates. Photomasks were prepared by a multifunction copying machine (Fuji Xerox, DocuCentre Color 450). The plates were irradiated with UV light (ultra high pressure mercury lamp, 75 mW/cm^2) for 6 s at 25°C through the photomask. The glass plate with the photomask was removed, and the other glass plate with a NIPAM gel dispersion layer was washed with distilled water to remove the unpolymerized parts. Thus, a glass plate with a pattern of a light-modulation layer was obtained. In the case of preparing multiple patterns, this process was repeated. PVA-SbQ solution was coated on the glass plate with specific patterns of the light-modulation layer at a thickness of 200 μm. The plate was exposed to UV light for 30 s and then covered with the second glass plate. Then, the edges of the glass plate were sealed with UV-curable adhesive. Thus, we obtained a light modulator with specific patterns.

Preparation of a thermosensor array

SDS (50, 100, and 150 m*M*) was added to dispersions composed of NIPAM gel particles (solid content: 2.3 wt %) and aqueous PVA-SbQ solution (5 wt %). SDS concentrations were 50, 100, and 150 m*M*, respectively. By using the photo-patterning procedure described earlier, three light-modulation layers with different SDS concentrations were fabricated on a glass plate. After forming the light-modulation layers, hydrophobic UV-curable resin was coated on the glass plate. Here, we used hydrophobic UV-curable resin to prevent the SDS concentrations from migrating among the light-modulation patterns. The glass plate was laminated with another glass plate and irradiated with UV for 30 s. The edges of the glass plates were sealed with UV-curable resin. Thus, we obtained a thermosensor array. The thermosensor array was heated on a hot plate, and the process of the color change was recorded by a digital camera (Fuji Film, FinePix F700).

RESULTS AND DISCUSSION

Photolithography is the process of transferring geometric shapes on a mask to a photoresist by irradiation with high-energy light such as UV light. Utilizing the photolithographic method, it is possible to draw a pattern with a high resolution, since the resolution is proportional to the exposure wavelength. We assumed that the patterns of LM gel could be fabricated by using a negative photoresist method. The negative resist becomes polymerized and more difficult to dissolve when exposed to UV light. The negative resist remains on the surface wherever it is exposed, and washing with solvent removes only in the unexposed portions.

There are two methods to form patterns constructed with LM gel: (1) A precursor solution of LM gel containing a monomer, crosslinker, pigment (colorant), and photoinitiator is coated on a substrate to form a pattern by UV irradiation through a photomask. (2) LM gel particles are dispersed in a negative photoresist solution. Then, a substrate is coated with the dispersion, and covered with a photomask to form patterns after UV irradiation.

Method 1 seems to be a direct and simple method. In fact, several researchers have developed similar methods to make stimuli responsive gel patterns for fabricating microvalves in microchannels[13] or artificial cilia.[14] However, when applying this method to synthesize LM gel patterns, there seem to be several shortcomings. The photoinitiator cannot start polymerization because of the high concentration of pigment, which absorbs UV light needed for radical generation. In addition, the LM gels peel away from the substrate during repetitive shrinking and swelling. On the other hand, we have already confirmed that stimuli responsive gel particles can be held tightly in photopolymer matrix and show volume changes with high durability.[15] Therefore, we chose Method 2.

We used NIPAM gel particles, well-known as thermoresponsive gel, containing pigments as colorants. NIPAM gels shrink above their lower-critical-solution temperature (LCST, 34°C) and swell below the LCST. Thus, a device using colored NIPAM gel will be colored or bleached, below and above the LCST, respectively. As a photoresist, we used poly(vinylalcohol)-styrylpyridinium (PVA-SbQ), which is water soluble and highly photosensitive.[16]

Figure 1 illustrates the process of the photo-patterning. Colored NIPAM gel particles were dispersed in aqueous PVA-SbQ solution (5 wt %) in the presence of 50 m*M* of sodium dodecyl sulfate (SDS) as a dispersant. SDS has also been reported to increase the LCST of NIPAM gels.[17–19] In this solution, the LCST of the NIPAM gel particles was around 44°C because of the effect of SDS.[15] The dispersion of the NIPAM gel particles was sandwiched between a glass plate and another glass plate with a photomask. The laminate was irradiated for 6 s thorough the photomask with UV light, which cured the PVA-SbQ below the open area of the photomask. After the UV irradiation, a patterned area constructed from NIPAM gel particles was imbedded in the cured PVA-SbQ matrix (we call it gel-in-gel composite, hereafter) was obtained. Then, the glass plate with the pattern was covered with another glass plate and the edges of the glass plates were sealed with UV-curable adhesive.

Figure 2 shows examples of fabricated patterns of the gel-in-gel composite. We found that the photomask pattern was precisely transferred as a light-modulation

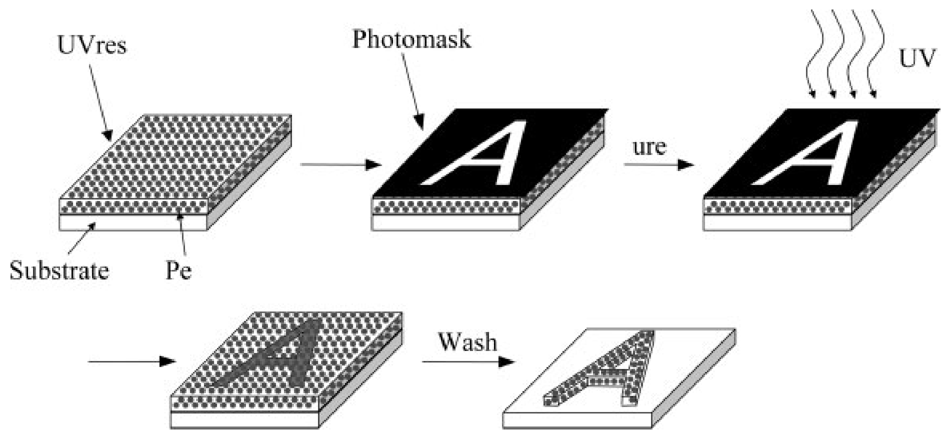

Figure 1 Schematic drawing of the process of fabricating a pattern constructed with PVA-SbQ and colored NIPAM gel particles.

layer in the gel-in-gel composite. As shown in Figure 2(a) and (b), the word ''GEL'' changed color density as the temperature changes. At 25°C, below the LCST of the NIPAM gels, the word was densely colored. At 60°C, above the LCST, the color of the word faded. This color-density change was caused by the alteration of the light-absorption area with volume change of the NIPAM gel particles. The word did not disappear completely at higher temperature, however, because above the LCST of the NIPAM gel, densely colored NIPAM gels existed in the pattern in their shrunken state.

When using this patterning technique to fabricate a display device, it is preferable for the patterns to disappear completely. This can be achieved if the color of the patterned area at its bleached state and the surrounding area of the pattern are designed to be the same. We fabricated such a light modulator by placing colored acrylamide gel dispersed in PVA-SbQ matrix around the patterned area [Fig. 2(c) and (d)]. In this light modulator, the pattern was clearly defined at a lower temperature. At higher temperatures, the color of the patterned area was faded and became almost the same color density of the surrounding area. Consequently, the word ''GEL'' became difficult to recognize with the naked eye. This method is suitable for various display devices, although the total transmittance of the light modulator decreased to some extent. Expanding this design concept, a light modulator that exhibits a pattern in the shrunken state of the gels and no pattern in the swollen state can be fabricated by making the color of the surrounding area the same as that of the swollen state of the gels.

To confirm the resolution of this method, a line pattern with different widths was prepared [Fig. 2(e)]. The line pattern could be resolved to around 200 μm using a simple photomask and UV-irradiation system. Generally speaking, the resolution of a photo-pattering is determined by the sensitivity of the photoresist to the wavelength of the light used for curing. In this patterning method, however, the resolution limit of the patterns was dominated by both the sensitivity of the photoresist and the diameter of gel particles, because the width of a pattern must be wider than the diameter of the gel particles and it determines the light-absorption path length. Currently, the diameter of the gel particles was ~30 μm to obtain sufficient color density. Therefore, the resolution limit was considered to be around 100 μm. A higher-resolution pattern using the gel particles could be formed when the size of the gel particles decreased and the concentration of colorant in the gel increased, because the minimum resolution of PVA-SbQ is below 10 μm.

By repeating the patterning process shown in Figure 1, light modulators with each patterning area containing different kinds of gel particles were fabricated. Figure 3 shows light modulators with different color patterns. Such light modulators with different colors may be useful for display objects with various letters or designs. In addition, a color filter using the gel particles with three primary colors was fabricated. In this study, we used thermoresponsive NIPAM gels; thus, this color-filter changed its color density according to temperature changes. It has been established that several kinds of stimuli responsive gels can respond to electricity. Therefore, it may be possible to develop reflective displays or color filters with variable color density using this photo-patterning method.

An additional demonstration of the versatility of this approach is the development of a sensor array. Utilizing the previously described patterning techniques, gel-in-gel composites that respond to different kinds or strength of stimuli can be formed on a substrate. It is known that the volume-change temperature, LCST, of

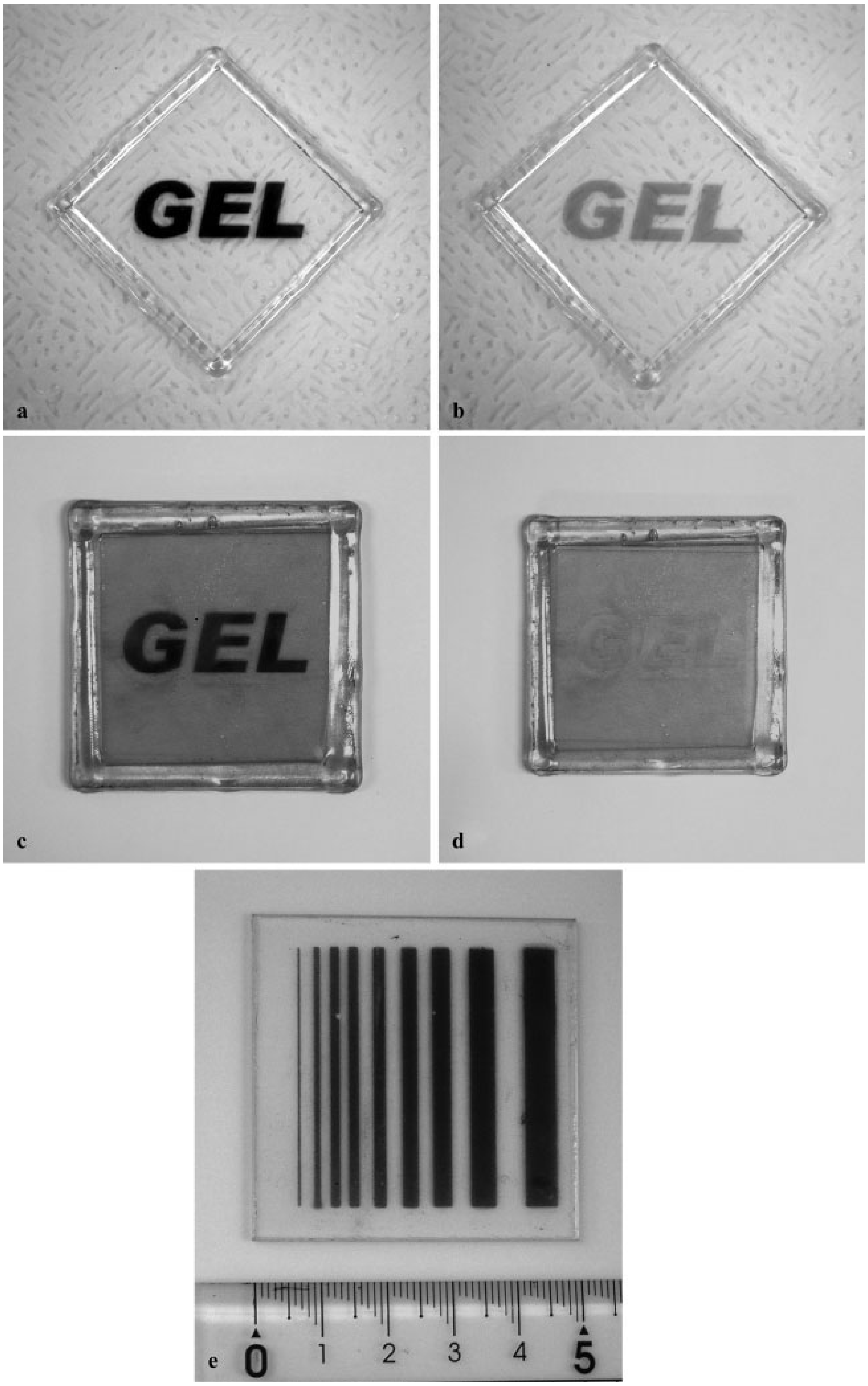

Figure 2 Light modulators with patterns constructed with PVA-SbQ and colored NIPAM gel particles: (a) colored state, 25°C, (b) bleached state, 60°C. In panels (c) colored state, 25°C, and (d) bleached state, 60°C, the area surrounding pattern was colored with black AAm gel dispersed in PVA-SbQ matrix. Panel (e) shows a line pattern to demonstrate the minimum resolution width. The size of each light modulator was 5×5 cm^2.

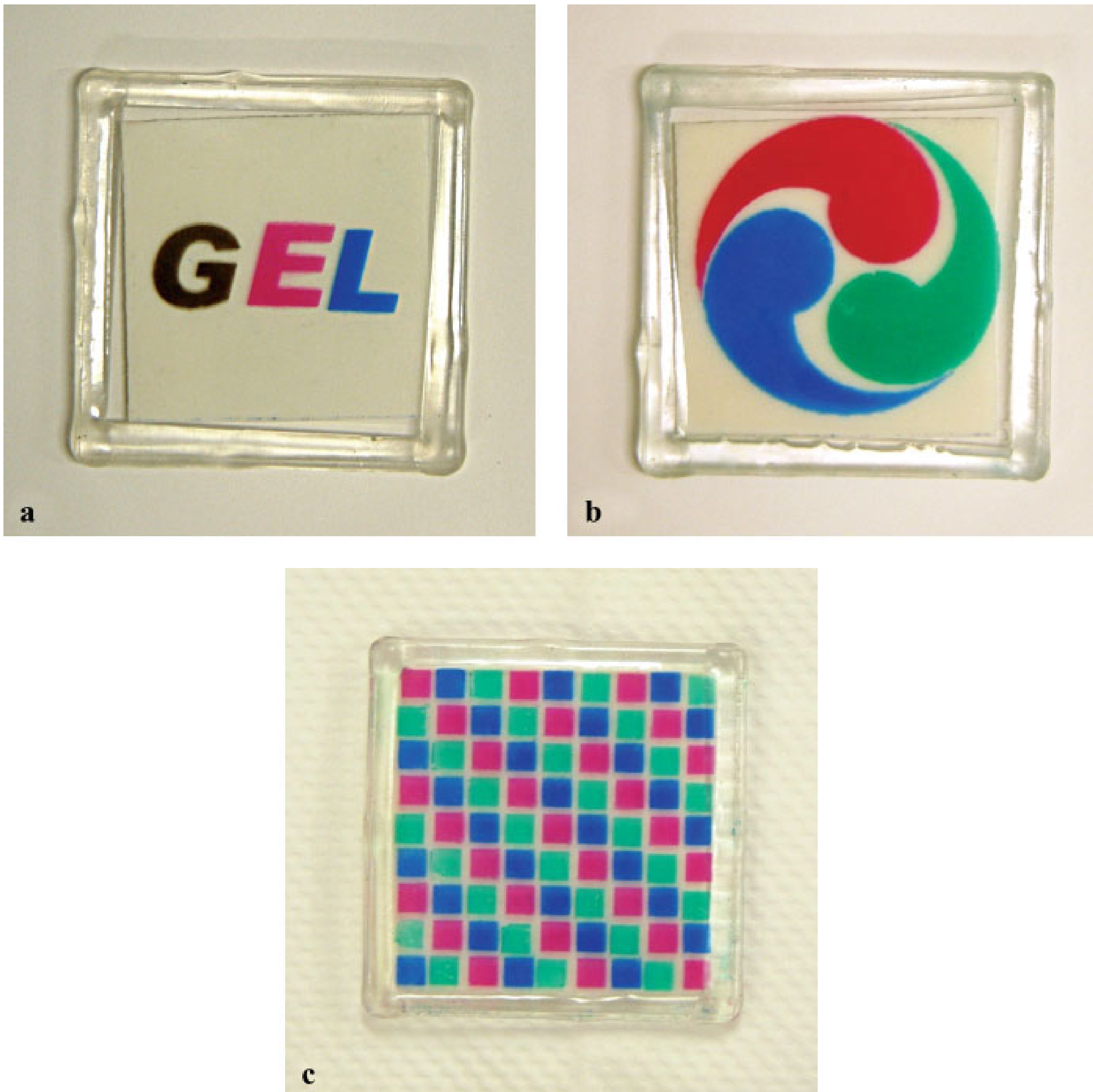

Figure 3 Light-modulation devices with patterns that contain different colors of NIPAM gel particles. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

NIPAM gel can be altered by concentration of SDS in the PVA-SbQ matrix. We attempted to fabricate a thermosensor array by forming three independent patterns on a glass plate, each of which contained different concentration of SDS. The concentrations of SDS in the patterns from the left were 50, 100, and 150 m*M*, and the LCSTs of the NIPAM gel particles were 44, 56, and 66°C, respectively. The sensor array was heated on a hot plate. Figure 4 shows the process of color-change of the thermosensor array. At ambient temperature, all the patterns were densely colored. With increasing temperature, the color of the sensor array faded, in order, beginning with the domain containing the lowest concentration of SDS (from the left to the right). When the temperature of the hot plate was raised to 75°C, all the colors were bleached.

The photo-patterning method has potential for use in various types of sensor arrays, because several domains, each containing stimuli responsive gel, respond to different strengths of stimuli. It has been reported that stimuli responsive gels can respond to various types of chemicals, such as pH, various metal ions,[20] and organic molecules like glucose.[21,22] Thus, various types of simple sensor arrays can be developed using the method studied in this article.

CONCLUSIONS

In this study, we demonstrated a new photo-patterning process to fabricate patterns of light-modulation layers constructed with colored NIPAM gel particles

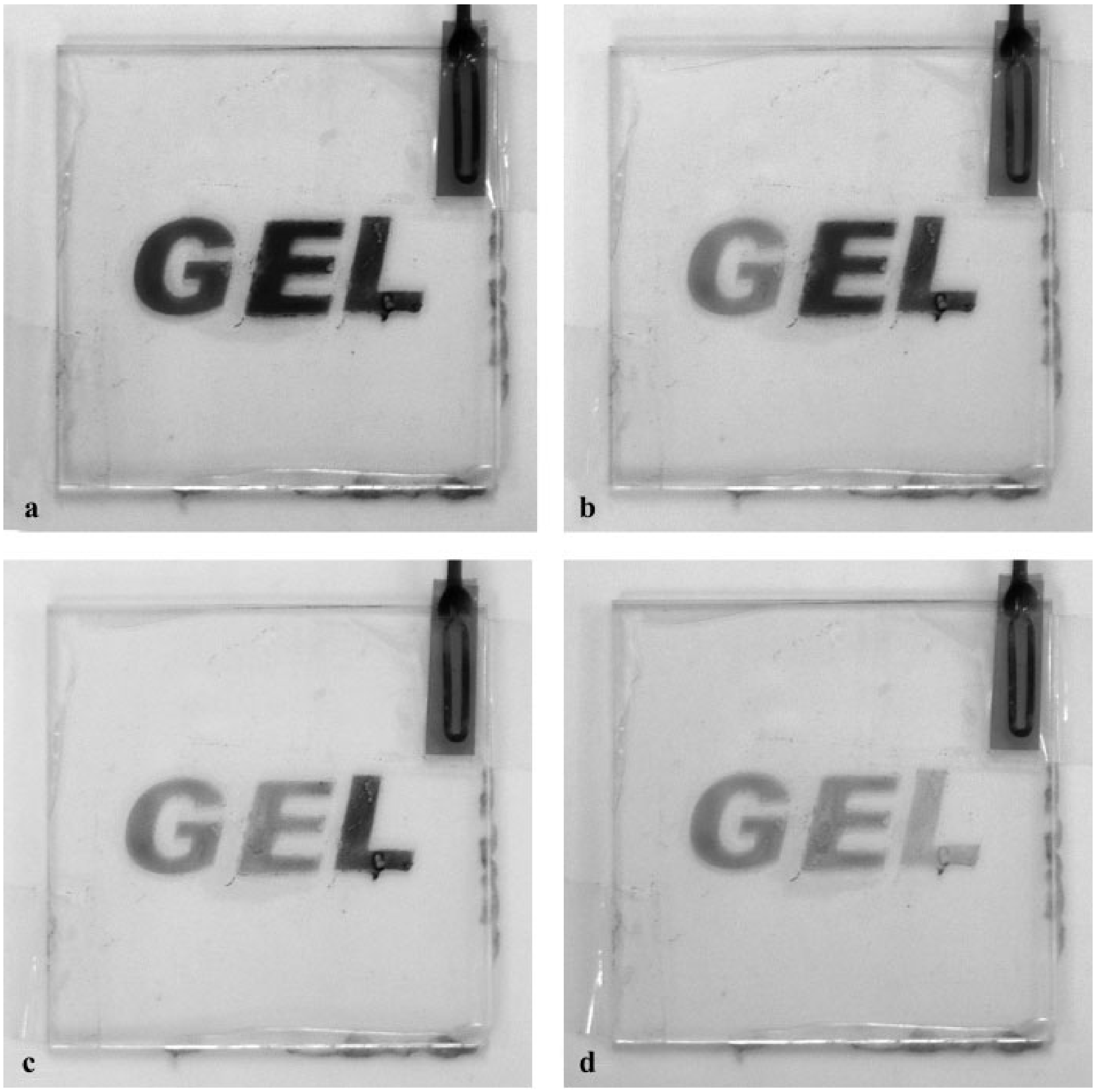

Figure 4 Thermosensor array utilizing NIPAM gel particles with different volume change temperatures made by adjusting SDS concentrations. SDS concentrations were 50 m*M* (G), 100 m*M* (E), and 150 m*M* (L). Temperatures of the hot plate were: (a) 30, (b) 50, (c) 60, and (d) 75°C, respectively.

and a PVA-SbQ gel matrix. Light-modulation patterns with a resolution of 200 μm can be formed with a simple photomask and UV-irradiation system. By repeating the photo-patterning process, light-modulation patterns were constructed with several domains, each of which contained different NIPAM gel particles. Display devices with different colors were prepared by patterning various colors of NIPAM gel independently. We also fabricated a thermosensor array utilizing NIPAM gel having different volume change temperatures. Our light-modulation gel has various advantages like freedom of color choice and excellent light-modulation properties. Thus, we believe that the photo-patterning approach described here has a strong potential to expand the applications of light-modulation gel. We plan to develop display devices utilizing electric-responsive gels with three primary colors and various types of sensor arrays.

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