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An Electro- and Thermochromic Hydrogel as a Full-Color Indicator**

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Intense research has been carried out in recent decades to develop stimuli-responsive chromic materials[1–4] for application in smart windows, displays, and switches. To try to address the demand for these applications, many researchers have focused on materials capable of being tuned into a variety of colors by means of external stimuli. Photonic crystals that are three-dimensionally periodic on a length scale comparable to the wavelength of light must be considered promising candidates for stimuli-responsive, full-color chromic materials. The color of the crystals is caused by a photonic bandgap (PBG) that forbids the propagation of electromagnetic waves in a certain frequency range.[5,6] It is technically possible to control the energy levels in the PBG by changing the periodicity and the average dielectric constant of the photonic crystals. Indeed, a close-packed colloidal crystal (CCC), which is self-assembled from monodisperse colloidal particles, offers a simple route to the fabrication of photonic crystals and can produce many desired colors.[7–10] The CCC appears to be a powerful tool for preparing stimuli-responsive chromic materials.[11–15]

Since a face-centered cubic (fcc) structure is generally the most energetically stable for the CCC,[16] and the CCC we prepared is oriented with its (111) axis parallel to a supporting glass substrate, the peak position of the PBG ($\lambda_{\max}$) for the CCC is obtained by[10]

$$\lambda_{\max} = 1.633(d/m)(n_a^2 - \sin^2\theta)^{1/2} \qquad (1)$$

where d is the diameter of the colloidal particles used, m is the order of the Bragg reflection, n_a is the refractive index of the CCC,[17] and θ is the angle measured from the normal to the plane of the CCC. Under normal incidence, Equation 1 can be rewritten as follows:

$$\lambda_{\max} = 1.633(d/m)n_a \qquad (2)$$

As noted above, Equation 2 shows that changing the periodicity and the average dielectric constant, that is, the values of d and n_a, respectively, can control the peak value. Thus, the size of the particles and the dielectric constants of all building blocks forming the CCC are known as the two determining factors of the PBG. If we attempt to obtain a CCC displaying full color, that is, exhibiting a change in the peak value from 400 to 800 nm, by just changing n_a, the value of n_a must be changed by a factor of two. It is considerably difficult to accomplish such a major change in the refractive indices of materials by applying external stimuli. Indeed, there have been several reports on the development of stimuli-responsive photonic crystals by changing n_a in response to external stimuli. One of the simplest and most inexpensive methods is the application of an opal or inverse opal infiltrated with liquid crystal.[18–20] An applied electric field can change the orientation of the molecules in the liquid crystal and, thus, affect its optical properties between one state, in which the incident light is substantially transmitted, to another state, in which the incident light is substantially diffracted. This behavior affects the average refractive index of the liquid crystal, and the position of the PBG can be shifted. However, this approach has not achieved the development of full-color chromic materials.

"Soft photonic crystals" composed of periodic structured polymer gels make it easy to create materials that can produce full color.[21–23] We have been studying two types of soft photonic crystals: the opal type,[24–26] comprised of periodically ordered colloidal gel particles, and the inverse-opal type,[14–16,21–23,27] possessing a periodically porous structure. Here, we would like to explain the optical property of the latter soft photonic crystal because it is easier to prepare and more applicable to the development of full-color chromic materials. The peak position of the PBG of the periodically porous gel, which is obtained by the CCC as template, can be quantitatively estimated by Equation 3:

$$\lambda_{\max} = 1.633\{d(D/D_0)/m\}n_a \qquad (3)$$

where D and D_0 are the characteristic sizes of the gel in the equilibrium state in a certain condition and in the preparative state, respectively. Hence, D/D_0 is defined as the equilibrium swelling degree of the gel. The change in D/D_0 can be up to a

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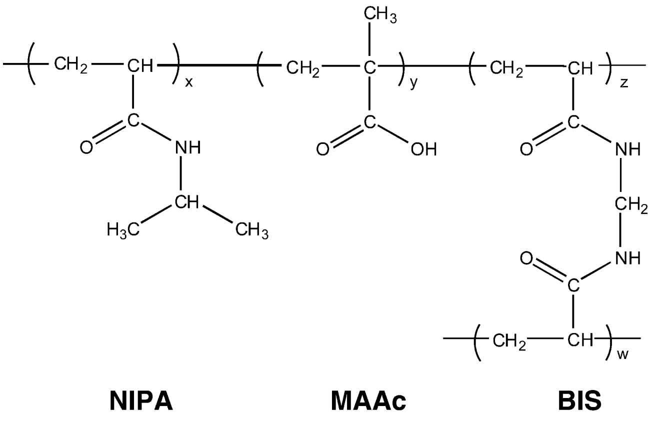
factor of 10.[28–31] The change in n_a for the inverse-opal-type periodically porous gel is vanishingly small when the volume undergoes drastic changes; the degree of swelling is dominant over λ_{max} of the observed reflection spectrum for the periodically porous gel.[23] As the periodicity of the porous gel ($d(D/D_0)$) can be easily controlled by various stimuli, the peak position of the porous gel is capable of being tuned in the whole visible region.

In this Communication, we present a periodically porous gel that exhibits various, switchable colors over the visible region initiated by both electrochemical reaction and temperature change. This gel displays every color in the visible region, depending on temperature. Moreover, this gel reveals an electrochemically triggered rapid two-state switching between two arbitrary structural colors at constant temperature.

To develop stimuli-responsive, full-color chromic materials, we need a material that exhibits a change of up to a factor of two in the linear swelling degree as a result of the effect of applied stimulation. To this end, we chose a pH- and thermosensitive polymer electrolyte hydrogel as the deformable soft material. We chose electrolysis of water by electrodes, which can control pH in aqueous solution, and temperature as the external stimuli. We prepared a copolymer electrolyte hydrogel of methacrylic acid (MAAc, as a pH-sensitive monomer), *N*-isopropylacrylamide (NIPA, as a thermosensitive monomer), and *N,N'*-methylene bisacrylamide (BIS, as a crosslinker) by free-radical polymerization (Scheme 1). This hydrogel exhibits different equilibrium degrees of swelling in response to pH as well as temperature.[32] By increasing the environmental pH above the pK_a of MAAc, which is copolymerized in the polymer network, to cause ionization of the carboxylic acid groups, the osmotic pressure is increased in the hydrogel and electrostatic repulsion is produced between the charges on the polymer network, causing the polymer network to expand and swell. Hence, a pH change induces swelling and shrinking of the hydrogel. Figure 1 shows an example of the pH-dependent swelling change of the hydrogel at 25 °C in various buffer solutions. At pH levels lower than 3.8, the swelling degree of the gel was about 1.15 and was almost independent of pH. This result suggests that most MAAc molecules in the polymer network exist as non-ionized carboxyl groups, and the gel behaves as a neutral network. As the pH was increased, the gel swelled drastically to about 1.67 (in D/D_0) at pH 8. Along with the increase in pH, the number of ionized carboxyl (carboxylate) groups on the network also increased, causing the polymer network to expand. Further increase in the pH caused the gel to swell further to about 1.72 in D/D_0 at pH 11.6, but the change in the volume was small above pH 7. The slight shrinkage of the gel at about pH 9–10 must be caused by the effect of some interaction between ionized carboxyl groups and cationic species in the ammonium buffer solutions.[33,34]



Scheme 1. Chemical structure of poly(NIPA-*co*-MAAc) gel.

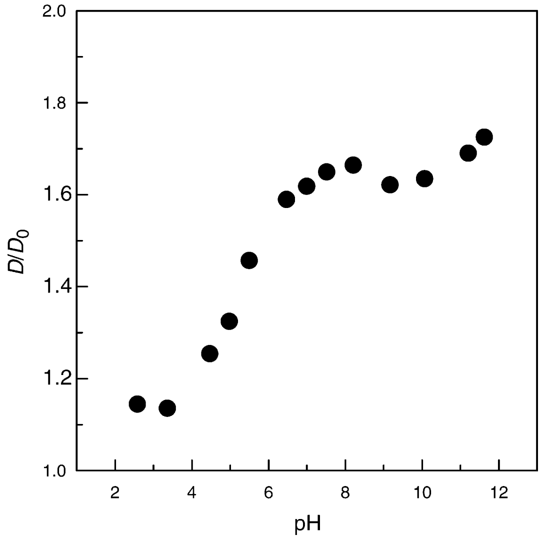


Figure 1. Equilibrium swelling ratio of poly(NIPA-*co*-MAAc) (90/10) gel as a function of pH in various pH buffer solutions at 25 °C. The ionic strengths of the buffer solutions are fixed at 50 mM.

Producing periodic porosity into this hydrogel using the CCC as a template provides us with an effective approach for creating a gel that exhibits various switchable colors over the visible region by external stimuli. Figure 2a shows the reflection spectra of the periodically porous gel composed of NIPA and MAAc in a HCl aqueous solution of pH 2.6 and at different temperatures. As the temperature increased, the reflected peak shifted to shorter wavelengths. This shift was due to the decrease in the lattice spacing of the fcc structure with the collapse of the gel. Figure 2b shows the measured λ_{max} and $\Delta\lambda/\lambda_{max}$ of the porous gel as a function of temperature, where $\Delta\lambda$ is the width at half-maximum of the peak. The experimentally obtained values of the peak wavelength exactly correspond to the value estimated by Equation 3, indicating that the porous gel maintains the fine structure of the precursor CCC, and the volume change is isotropic. The peak value of the PBG of this porous gel appeared in the range from 330 to 650 nm below the lower critical solution temperature (LCST) of this gel. If necessary, the range of peak wavelength reflected by the porous gel can be easily adjusted by changing the size of the silica particles or the composition of the pre-gel solution, for ex-

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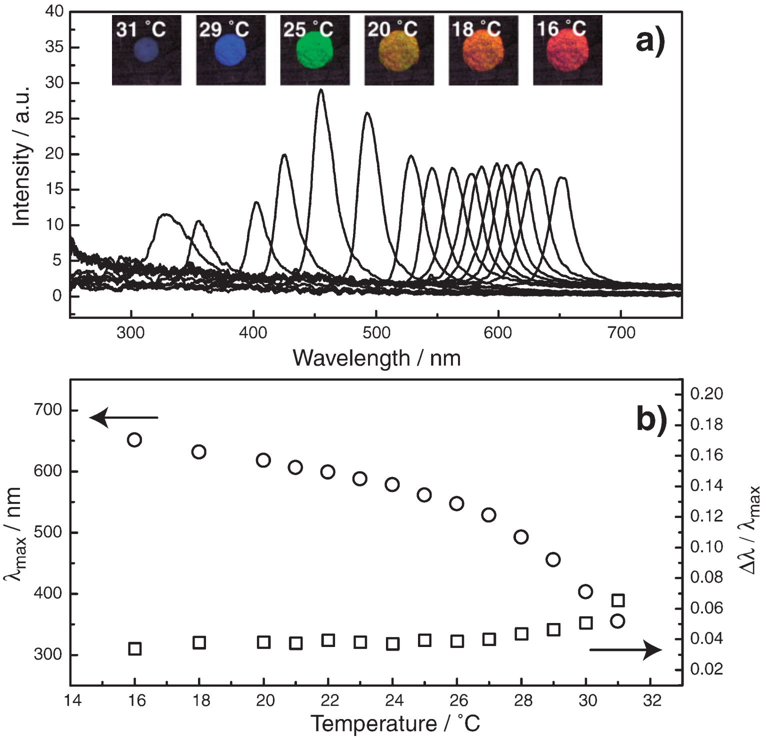

Figure 2. a) Reflection spectra of the porous poly(NIPA-*co*-MAAc) (90/10) gel in pH 2.6 HCl aqueous solution at various temperatures. Pictures show the change in color of the porous gel at different temperatures. b) Temperature dependence of λ_{max}, and $\Delta\lambda/\lambda_{max}$ of the reflection spectra, shown in (a), are plotted as a function of temperature.

ample, by changing the amount of crosslinker and the monomer concentration. The experimentally obtained values of $\Delta\lambda/\lambda_{max}$ for the porous gel explain its degree of deformation behavior;[23] a slight increase in $\Delta\lambda/\lambda_{max}$ could be observed near the LCST, while the value was almost constant below 25 °C, indicating that the deformation of the porous structure occurs with the volume shrinkage near the LCST. The introduction of the interconnecting periodic porosity into gels by using the CCC as a template induces rapid change in the volume as well as a chromic phenomenon in the gel.[35] Additionally, the coexistence of different volumes can be achieved in the porous gel, because the amount of elastic energy induced by the coexistence of different swollen states in the porous gel is much smaller than that in the homogeneous gel; the porous gel is simultaneously able to reveal multiple PBGs. Accordingly, the periodically porous gel composed of the NIPA–MAAc copolymer network has the potential to develop rapid switchable chromic materials in response to pH and temperature.

Because electrolysis of water causes a change in the pH of an electrolyte solution in the vicinity of the electrodes, the swelling degree of a pH-sensitive hydrogel that is placed on the electrodes can be easily and drastically changed by electrolysis. If a sufficient voltage, enough to electrolyze water molecules, is applied between the two electrodes in the electrochemical system used here, a rapid and reversible pH change will occur. It follows that a rapid and reversible change in the structural color can be observed in the porous gel placed between the electrodes. To simplify the scientific interpretation of the observed results, the porous disk-shaped hydrogel was placed on the anode. Before the voltage was applied, the pH surrounding the gel was about 6. When 1.8 V was applied across the electrode using a DC power supply, the pH decreased sharply and the solution became acidic at the anode. The emergence of bubbles during the electrolysis is seldom visible to the naked eye, because the gas-evolving reaction rate is slow under mild conditions; the electrolysis does not obstruct the optical observation of the porous gel. In our system, the pH in the vicinity of the anodic electrode, which is measured by a micro-pH electrode at a point about 1 mm away from the surface of the anode, reached a value of 3.8 within 15 min and remained at this value during electrolysis. As mentioned above, the volume of this gel is almost constant below pH 3.8. Consequently, it takes only a few minutes to reach the acidic condition in which a gel of 0.9 mm in thickness enters a collapsed state. Because, however, the change in pH is attributed to the production and diffusion of H^+ ions from the anode, a spatial–temporal change in pH around the porous gel can be observed during the course of the electrolysis.

This rapid, drastic, and spatial–temporal change in pH affects the kinetic change in the volume of the porous gel and causes the interesting two-state switching phenomenon in the reflection spectra. Figure 3a shows the kinetic alteration in the reflection spectra of the porous gel during electrolysis. Before electrolysis, the porous gel was transparent and colorless at 25 °C; the peak value of the reflection spectra could be observed at 800 nm. As electrolysis progressed in the primary stage, the peak intensity decreased dramatically, while the peak value remained at 800 nm. The reflected peak completely disappeared within a few minutes. After a period of time, the new peak appeared at 580 nm (Fig. 3a and b), and the peak intensity rapidly increased (Fig. 3a and c). Ultimately, the porous gel exhibited a brilliant green color, and the color did not change as long as electrolysis continued. In the initial stage during the two-peaks switch, the value of $\Delta\lambda/\lambda_{max}$ changed with an inverted V-shaped recovery (Fig. 3c). The decrease in the peak intensity and the increase in the value of $\Delta\lambda/\lambda_{max}$ are attributable to distortion in the porous structure.[23] This distortion may be induced by the difference in the sizes of various parts of the porous gel, because the relaxation time of the swelling and shrinking of a gel is proportional to the square of the characteristic size.[36]

In this system, which demonstrates the two-state color switching induced by electrochemical reaction, the mechanism of the swelling change of the porous gel, associated with a spatial–temporal pH change, can be considered to have the following three stages: 1) The solution pH on the surface of the anode instantaneously fall below 3.8 by electrolysis. It fol-

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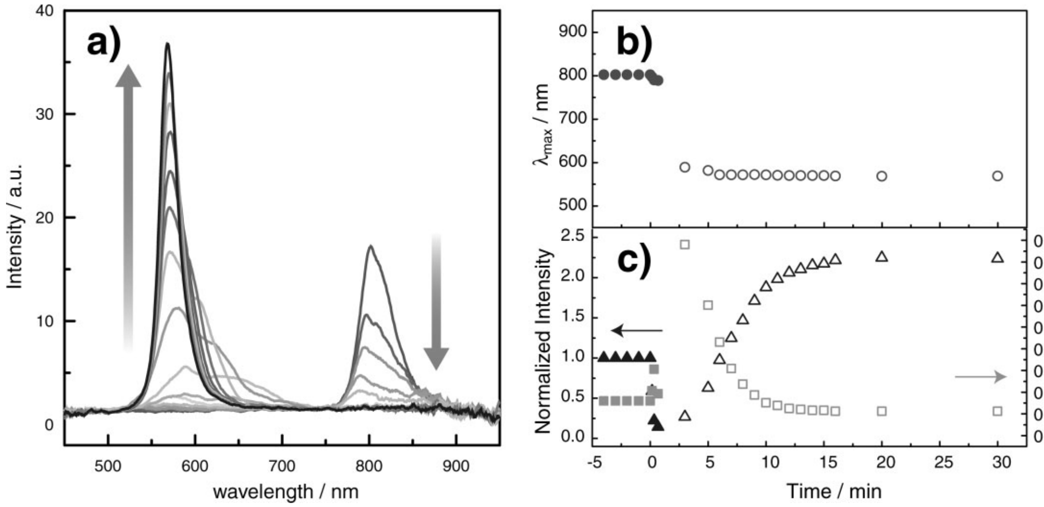

Figure 3. a) Dynamic change in reflection spectra of the porous poly(NIPA-*co*-MAAc) (90/10) gel in the shrinking process induced by electrolysis at 25 °C. The spectral parameters, which are b) λ_{max}, c) normalized intensity (triangles), and $\Delta\lambda/\lambda_{max}$ (squares), plotted as a function of time in the shrinking process during electrolysis. Solid marks indicate information for the reflection spectra at 800 nm, and open marks describe the information for the newly appeared reflection spectra at 580 nm. Arrows indicate the direction of change.

lows that a pH gradient along a direction perpendicular to the anode develops from the electrode surface; the porous gel collapses from the surface of the gel attached on the anode, and reveals an anisotropic swelling change (Fig. 4a). This change induces the decrease in the peak intensity of the reflection spectra of the porous gel. 2) The thickness of the diffusion layer of H^+ along the direction perpendicular to the anode grows with time. Then, the whole porous gel is surrounded in the pH gradient. Since the porous gel takes on an awkward shape (Fig. 4b), the gel loses the ability to reflect light following Bragg's law. 3) The pH value of the solution surrounding the gel goes below 3.8, after sufficient time; the swelling degree of the gel gradually reaches the equilibrium collapsed state from the side attached on the anodic electrode to the other side (Fig. 4c). As a result, the peak intensity of the new reflected spectrum increases.

This two-state color switching can also be observed at different temperatures (Fig. 5). Judging from the observation of the cross-sectional shape of the porous gel during the volume change, bending behavior can be seen in cases with a substantial change in λ_{max}. Additionally, the colors from the gel can be recovered by reversing the applied voltage (Fig. 6a–c). An overshoot phenomenon in λ_{max} could be observed after reversing the applied voltage, because the pH value of the solution surrounding the gel became weakly basic in the initial stage and then returned to 6 (Fig. 6d).

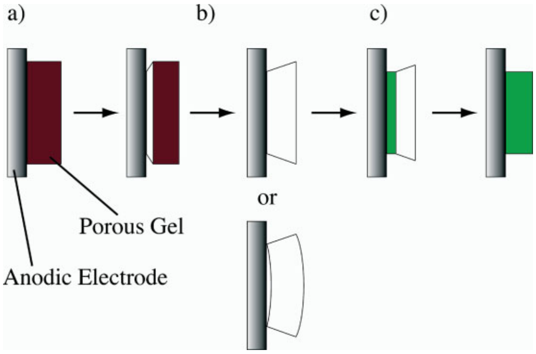

Figure 4. Dynamic shape variation of the porous gel on the anodic electrode during electrolysis. Each state is described in the main text.

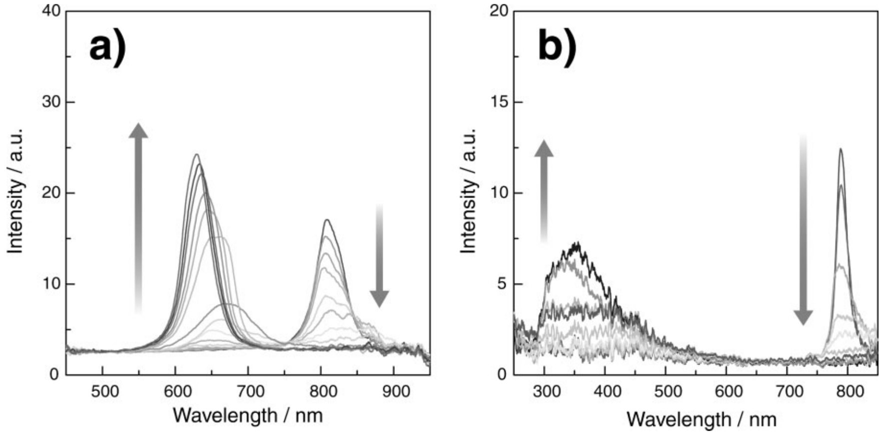

Figure 5. Temperature dependence of the dynamic change in reflection spectra of the porous poly(NIPA-*co*-MAAc) (90/10) gel in the shrinking process induced by 1.80 V application at a) 21 °C, and b) 31 °C. Arrows indicate the direction of change.

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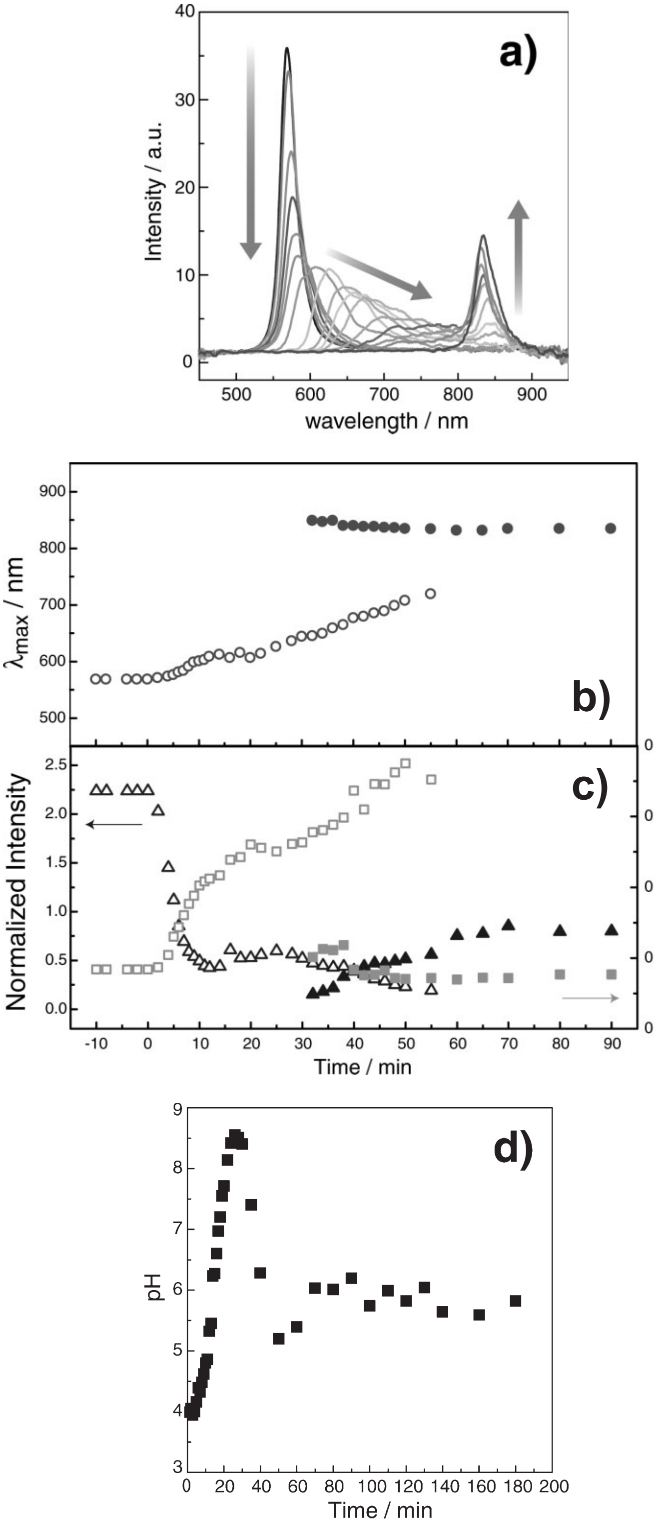

Figure 6. a) Dynamic change in reflection spectra of the porous poly(NIPA-*co*-MAAc) (90/10) gel after the polarity of the electrode is reversed. The spectral parameters, which are b) λ_{max}, c) normalized intensity (triangles), and $\Delta\lambda/\lambda_{max}$ (squares), plotted as a function of time in the swelling process during electrolysis. Solid marks indicate information for the newly appeared reflection spectra at about 800 nm, and open marks describe the information for the reflection spectra at about 580 nm. d) Change in pH with time at a point 1 mm from the carbon electrode after reversing the polarity of the electrode. Arrows in (a) indicate the direction of change.

It is known that there is an approach that couples the mechanochromic response of the PBG with the intrinsic electroactive properties of dielectric, soft materials to tune the position of the PBG by an applied electric field.[37] The electrochemical control of the position of the PBG for a PBG composite composed of close-packed silica colloidal crystals and a crosslinked redox-active polymer matrix has also been attempted.[38] Although these systems are examples of the approach to controlling the position of the PBG by changing the periodicity, these systems exhibit continuous "shifts" in the peak color and cannot bring about the major change in the position of the PBG necessary to describe full color, as the change in the interplanar distance for these systems cannot reach a factor as large as two. In contrast, our newly developed stimuli-responsive chromic hydrogel exhibits an electric-field-triggered "two-state switching" between two arbitrary structural colors in the entire visible region at certain temperatures. The external rapid tuning of the structural color of this new soft material in the entire visible region has been successfully achieved by introducing the periodic, ordered interconnecting porous structure into the pH- and thermosensitive hydrogel. Although, there is still room for improvement, such as angle dependence in color and the response speed for applications like displays and switches, this multicolor chromic soft material controlled by dual stimuli is a conceptually new approach to the fabrication of full-color display materials by means of electric and thermal stimuli.

Experimental

Materials: NIPA, courtesy of Kojin Co., Japan, and *N*,*N*′-azobis (isobutyronitrile) (AIBN), purchased from WAKO Pure Chemicals, were purified by recrystallization in a toluene/hexane mixture and in methanol, respectively. MAAc, from WAKO Pure Chemicals, BIS, from Aldrich, and a silica colloidal suspension, from Nippon Shokubai Co. (diameter = 210 nm, 20 wt % solid), were used as received.

Preparation of the Cylinder-Shaped Gel: For the swelling measurement, the cylindrical bulk copolymer gel of NIPA and MAAc was obtained by free-radical copolymerization. The monomer concentrations of NIPA and MAAc were 1.44 M and 0.16 M, respectively, and 4 mol % of BIS and 1 mol % of an initiator, AIBN, versus the total monomer concentration (1.6 M) were dissolved in degassed and nitrogen-saturated ethanol. Polymerization was performed in a micropipette of 280 μm inner diameter at 60 °C for 24 h. The cylindrical polymer gel was removed from the micropipette and repeatedly washed with a large amount of distilled water. The gel was then washed with 1 mM HCl aqueous solution to completely convert the carboxyl groups on the polymer network into an acidic form. After that, the gel was purified

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against a large amount of distilled water to remove the excess amounts of HCl.

Preparation of the Porous Gel: The close-packed silica colloidal crystal (CCC), used as a template to make the porous gel, was formed by the self-assembly of silica spheres 210 nm in diameter using the monodisperse silica colloidal suspension and a glass plate as a supporting substrate. The aqueous solvent in the colloidal suspension was evaporated at 100 °C in a thermostatic chamber after the colloidal suspension was cast onto the 76 mm × 52 mm glass substrate. Utilizing this simple method, we could easily obtain a CCC possessing a certain measure of thickness (~ 500 µm) for the template synthesis. After that, the pre-gel solution composed of the same components as the cylindrical gel was infiltrated into the voids of the CCC in a petri dish, and the polymerizations were conducted at 60 °C for 24 h. The resulting gel with involvement of CCC was immersed in a 5 wt % HF aqueous solution for one week to remove the SiO_2 component. The porous gel membrane that was obtained was washed carefully with a large amount of distilled water to remove HF and other impurities, and was then washed repeatedly in the same way as the purification of the cylindrical gel was performed.

Swelling Measurement for the Cylindrical Bulk Gel: In the pH-dependent swelling measurement, pH was adjusted by varying the buffer solutions. We used three types of buffer solutions, the ionic strengths of which were fixed at 50 mM: namely, these were phosphate (in pH range from 2.5 to 3.5, from 6.5 to 8.5, and from 11 to 12), acetate (in pH range from 4 to 6), and ammonium (in pH range from 9 to 10) based buffers. By monitoring the equilibrium diameter of the cylindrical gel, D, in various buffer solutions using an optical microscope (Nikon TMS-F) with a calibrated scale, the swelling ratio of the gel, D/D_0, was determined, where D_0 was 280 µm. The temperature of the buffer solution was maintained at 25 °C by a circulating water system.

Reflection Spectroscopy of the Porous Gel: The disk-shaped porous gel, which was cut from the porous gel membrane, was used as a sample for this measurement. An Ocean Optics USB2000 fiber-optic spectrometer was used with a tungsten halogen lamp (Ocean Optics, Inc., LS-1) or a deuterium tungsten halogen lamp (Ocean Optics, Inc., DT-MINI) as a light source. The structural color of the porous gel was observed with a digital microscope (KEYENCE VH-8000). To measure the reflection spectra of the porous gel during water electrolysis induced by applied voltage, a carbon working electrode (Nilaco Co.) (geometrical area: 7.3 cm^2), a Au counter electrode, and 40 mL of 16.7 mM Na_2SO_4 aqueous solution, as an electrolyte solution, were used. The disk-shaped, porous poly(NIPA-*co*-MAAc) (90/10) gel was washed repeatedly with the Na_2SO_4 electrolyte solution to achieve the equilibrium condition before the measurements were carried out. The resulting sample gel had a diameter of 2.65 mm and a thickness of 0.90 mm in the Na_2SO_4 aqueous solution at 25 °C. The porous gel was placed on the carbon electrode, and reflection spectroscopy was dynamically performed. The changes in color, figuration, and size of the porous gel were also measured dynamically with the digital microscope. The temperature dependence of the optical properties was measured by controlling the temperature of the electrolyte solution with a water circulating system.

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