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Optoelectronics

Electrically Tunable Hysteretic Photonic Gels for Nonvolatile Display Pixels**

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Materials that display hysteresis, such as ferromagnetic or ferroelectric materials, have been extensively investigated for their potential engineering applications towards electromagnetic memory devices and switches. While similar hysteretic volume phase transitions are observed in many soft organic materials, including hydrogels[1] and biomaterials,[2] it has not been well exploited but is often considered as problematic because it complicates the calibration procedure and affects signal reproducibility in many conventional applications of hydrogels in sensors and drug delivery.[3] However, such hysteretic volume phase transitions of hydrogels can be utilized in a positive way when they are combined with other functional materials and carefully tuned to exhibit strong bistability. For example, Kim et al. recently reported wet photonic gel memory pixels by combining the hysteresis of hydrogels with photonic crystals.[4] Block copolymer photonic gels consisting of alternating glassy polystyrene (PS) and swellable poly(2-vinyl pyridine) (P2VP) gel layers showed pH-dependent photonic stop bands. The optical responses of the photonic gels varied with the direction of pH changes. This hysteretic optical response of photonic gels was able to be tuned and further optimized by controlling ion-pairing affinity between the protonated pyridine groups and their counteranions.

Extending the previous work, herein we report electrochemically controllable nonvolatile photonic pixels and their applications towards e-papers. Our approach is clearly different from the nonvolatile photonic ink demonstrated by Ozin and co-workers[5] in the sense of using hydrogel hysteresis instead of using redox reaction of metallopolymers. Electroactive photonic pixels were achieved by coupling the hysteretic optical properties of PS-*b*-P2VP block copolymer photonic gels to the electrochemical cells, where the pH gradient can be tuned. Similar to other conventional hydrogels,[6] our photonic gels show volume expansion and contraction in response to the applied electric field, and accordingly exhibit various photonic colors.[7] We assumed that electroactive nonvolatile photonic gels can be achieved when the volume transition of gel layers was tuned to exhibit strong hysteresis with changes of electrochemically driven pH gradient.

The electroactive photonic pixel comprises a simple electrochemical cell consisting of two transparent electrodes separated by 1 mm thick spacer and electrolytes (Figure 1 a). The block copolymer photonic gel films were coated on the working electrode. The block copolymer photonic gel films were prepared as previously described.[4,7–8] Briefly, in-plane oriented lamellar films were first prepared by spin casting

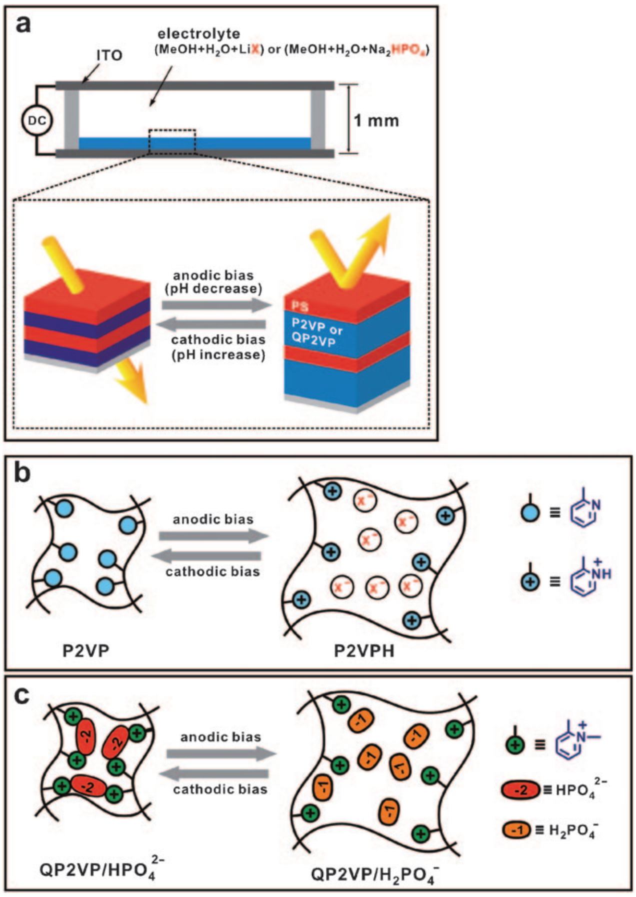

Figure 1. Schematic structure of photonic pixel and proposed mechanisms for gel swelling and deswelling by an electrically induced pH gradient.

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PS_{57}-*b*-$P2VP_{57}$ solution ($M_n \times 10^{-3} = 57/57$, PDI = 1.08, 6 wt% in propylene glycol monomethyl ether acetate) onto indium tin oxide (ITO) glass followed by annealing the films in chloroform vapor at 50 °C for 2 days. The thickness of the films was controlled to approximately 1 μm. The photonic gel films were then assembled into the electrochemical cells filling with various electrolytes, mixtures of methanol and water (volume ratio of methanol/water = 99:1) containing salts such as LiCl, LiBr, $LiBF_4$, or $LiOOCCH_3$ ($c = 0.5$ mM). The trace amount of water in the electrolytes was added to increase the solubility of salts in methanol and to develop a pH gradient by electrolysis of water. Hydronium and hydroxide ions can be produced by electrolysis of water and their movement toward the counter electrodes induce a pH gradient within a cell.[9] By using pH-sensitive organic dyes,[9b,10] we confirmed that the pH value can be modulated to as low as pH 2.5 at the anode side and as high as pH 12 at the cathode side when the bias voltage was between 0 and 5 V. At this condition, the pyridine groups in P2VP layers (apparent pK_a of protonated P2VP, $pK_{a,P2VPH} \approx 3.2$) can be protonated with application of anodic bias voltage, and the resultant pyridinium groups pair with anions of electrolytes, which are attracted to the positively charged electrode (Figure 1 b).[4] The reverse processes also occur with application of cathodic bias voltage.

The PS-*b*-P2VP photonic gel films swollen with electrolytes originally exhibited a violet photonic color ($\lambda_{max,0V} = 388$ nm) at zero bias voltage (Figure 2). The photonic gel films gradually turned green upon application of anodic bias voltage at the working electrode. The position of photonic stop band shifted to $\lambda_{max,+5V} = 572$ nm the bias voltage was increased from 0 to +5 V when LiCl was used as electrolyte. Photonic pixels showed a turn-on voltage at between +1 and +2 V, which is close to the reduction potential of water ($E° = 1.23$ V at pH 7).[11] We attribute the red-shift of photonic stop bands to the protonation of pyridine groups in P2VP layers, which induces the volume expansion of P2VP layers by ionic repulsion (Figure 1 b).[7,12] The red-shifted photonic stop bands gradually relaxed to the original position ($\lambda_{max,0V} = 388$ nm) upon removal of the bias voltage. The relaxation of the photonic stop bands was highly dependent on the species of electrolyte. For quantitative analysis, the half relaxation time ($\tau_{1/2}$), which is defined as the time elapsed until the photonic stop bands become $\lambda_{max} = (\lambda_{max,0V} + \lambda_{max,+5V})/2$ after application of an anodic pulse voltage (+5 V for 3 s), was measured for several electrolytes (Figure 3). The relaxation was very fast for $LiOOCCH_3$ ($\tau_{1/2} = 3$ s) but it was much slower for LiBr ($\tau_{1/2} = 20$ min). For a given set of experiments, the relaxation time increased in the order of $LiOOCCH_3$ ($\tau_{1/2} = 3$ s) < LiCl ($\tau_{1/2} = 1$ min) < $LiBF_4$ ($\tau_{1/2} = 4$ min) < LiBr ($\tau_{1/2} = 20$ min). This behavior can be interpreted in terms of the hysteresis strength. As shown in Figure 4, the red-shifted photonic stop bands at pH_{+5V} relax to the point of pH_{0V} following the hysteresis loop upon removal of the bias voltage. In this case, the faster relaxation is expected when the hysteresis loop deviates more from the point of $pH_{0V} \approx 7.2$. This behavior is well supported by the fact that the order of relaxation time corresponds to the order of the hysteresis strength of the photonic gels dependent on anions.[4] Following our hypothesis, it is expected that the nonvolatility in photonic pixels can be improved either by lowering the pH_{0V} value to be close to the conversion pH (pH_c) of hysteresis loop or by shifting hysteresis loop close to pH_{0V} (Figure 4). While both methods were effective for

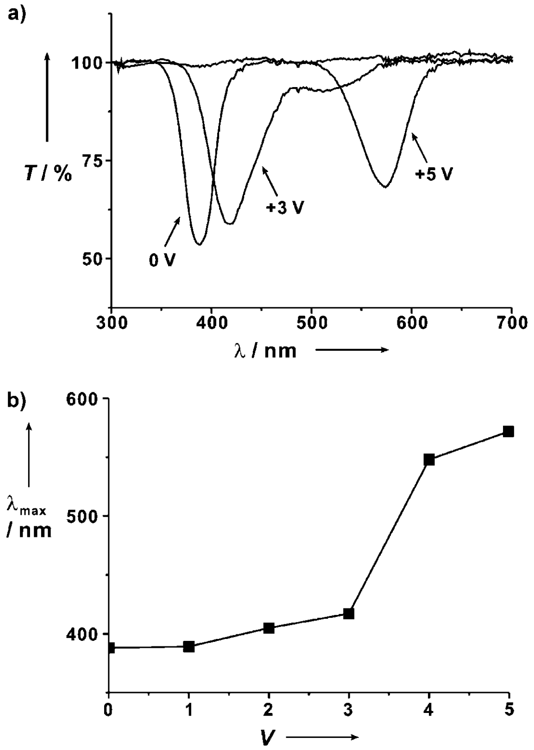

Figure 2. Optical responses of a PS-*b*-P2VP photonic pixel filled with LiCl electrolyte in response to the applied voltage (0–+5 V): a) UV/Vis transmission spectra and b) variation in λ_{max} with bias voltages.

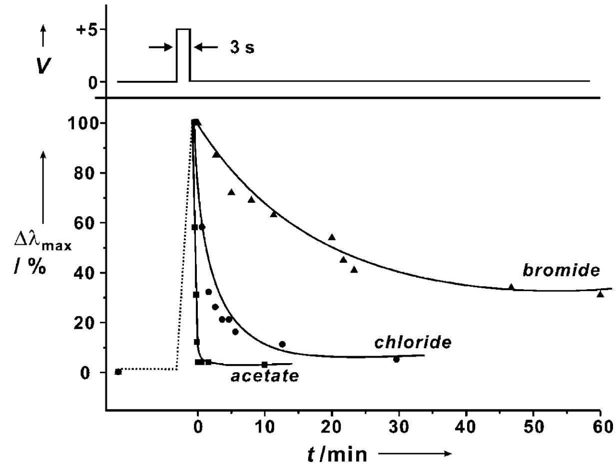

Figure 3. Anion-dependent relaxation of photonic stop band in PS-*b*-P2VP photonic pixels after application of a short pulse of bias voltage (+5 V for 3 s). Each pixel was filled with various electrolytes: LiCl, LiBr, and $LiCOOCH_3$. The peak shifts for each anion were normalized by taking the percent peak shift defined as $\Delta\lambda_{max} = [(\lambda - \lambda_{max,0V})/(\lambda_{max,+5V} - \lambda_{max,0V})] \times 100$.

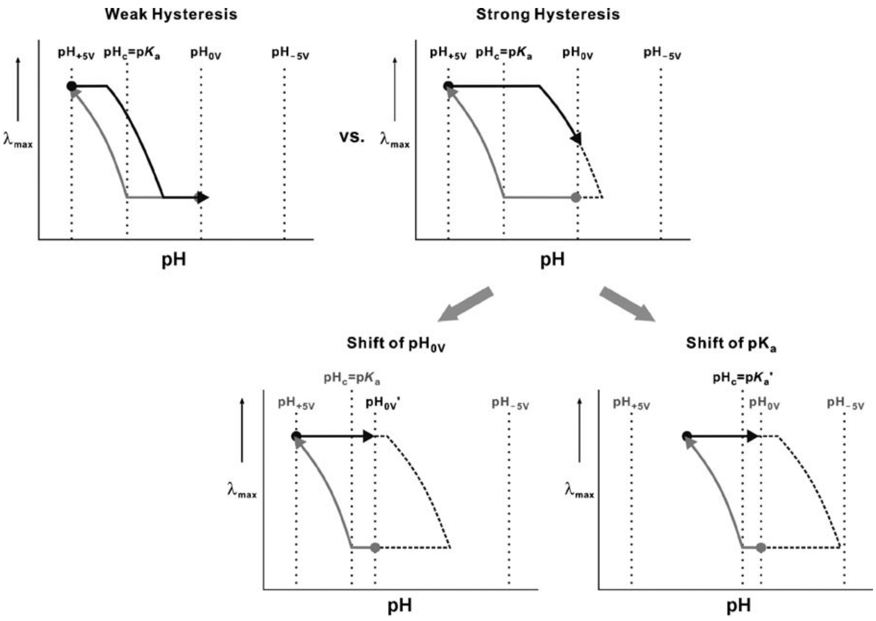

Figure 4. Effect of hysteresis on the nonvolatility of a photonic pixel.

increasing nonvolatility, we focused mainly on the latter because of its better cell stability.

Since the value of pH_c is determined by the pK_a value of the gel materials, the hysteresis loop of photonic gels can be shifted to a higher pH regime by using polymers with high pK_a values or by introducing protic anions with high pK_a values to the quaternized P2VP blocks (Figure 1c). To alleviate our efforts of synthesizing new polymers, photonic gels were modified with protic anions after quaternizing pyridine groups with iodomethane. Among many choices of anions, phosphate ion, a multiprotic anion, was chosen for our experiments because of its pK_{a2} value close to pH_{0V} ($pK_{a1} = 2.12$, $pK_{a2} = 7.21$, $pK_{a3} = 12.67$) and its capability of tuning photonic stop bands by ionic cross-linking and decross-linking. Since multivalent ions serve as cross-linkers for polyelectrolyte gels,[13] QP2VP gel layers shrink at $pH > 7.21$ as a result of ionic cross-linking induced by the formation of HPO_4^{-2}, and oppositely expand at $pH < 7.21$ owing to decross-linking induced by the formation of $H_2PO_4^{-1}$ (Figure 1c). Therefore, PS-*b*-QP2VP photonic gels modified with phosphate ions showed photonic color changes with pH as similar as PS-*b*-P2VP photonic gels, and a well defined hysteresis loop showing a pH_c value at 7.2 which corresponds to the pK_{a2} of phosphoric acid (Figure 5a).

The PS-*b*-QP2VP photonic pixels modified with phosphate ions originally exhibited a green photonic color at zero bias voltage, and then gradually turned red upon application of anodic bias voltage at the working electrode. The photonic stop band shifted from $\lambda_{max,0V} = 526$ nm to $\lambda_{max,+5V} = 610$ nm with increasing bias voltage from 0 to +5 V (Figure 5b,c). The photonic colors can be recovered to the original position by applying cathodic bias voltage (Figure 5c). The photonic color transition was reproducible up to a series of 30 anodic–cathodic bias cycles (+5 V–−5 V) (Figure 6). PS-*b*-QP2VP photonic gels modified with phosphate ions showed stable nonvolatile photonic colors in electrochemical cells because their pH_c value is close to the pH_{0V} value and they display moderately strong hysteresis. The red-shifted pho-

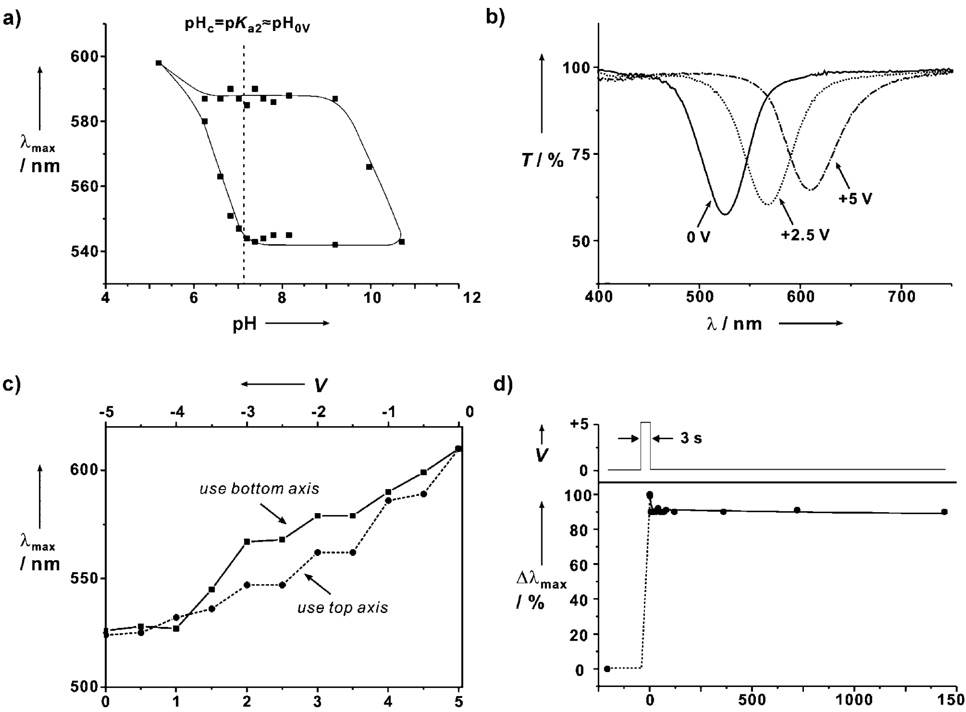

Figure 5. Optical properties of PS-*b*-QP2VP photonic pixels modified with phosphate ions: a) Hysteresis loop of PS-*b*-QP2VP photonic gel film modified with phosphate ions. The solution pH was varied by changing the ratio of Na_2HPO_4 and NaH_2PO_4. b) UV/Vis transmission spectra and c) variation in λ_{max} with bias voltages. d) Photonic stop band relaxation in PS-*b*-QP2VP photonic pixels modified with phosphate ions after the application of a short pulse of bias voltage (+5 V for 3 s; top).

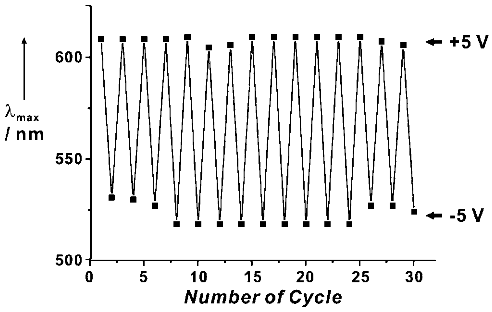

Figure 6. The stability of photonic pixels over a series of 30 anodic (+5 V)–cathodic (−5 V) bias cycles.

tonic color by application of the anodic bias was preserved when the bias was removed. Unless cathodic bias was applied, the photonic color was maintained for several days. As shown in Figure 5d, the relaxation time was measured to be longer than 25 h. Utilizing our findings, we demonstrated two different types of electrically tunable display pixels; one is volatile and the other is nonvolatile (see Movies S1 and S2 in the Supporting Information). Both pixels exhibited broad color tunability with the change of bias voltage. However, the photonic color in the pixel modified with acetate ions quickly vaporized (Movie S1) whereas the other pixel modified with phosphate ions persistently retained the color without bias voltage (Movie S2).

In summary, electrically tunable photonic pixels exhibiting nonvolatile photonic colors have been demonstrated using PS-*b*-P2VP block copolymer photonic gels. The optical volatility of photonic pixels was tuned by controlling the hysteresis strength and the position of pH_c, which were both highly dependent on the species of anions pairing with pyridinium groups. We anticipate that our results will provide useful information for understanding the volume transition of hydrogels under an electric field and suggest design rules for photonic display devices based on photonic crystals. In particular, the features of our photonic pixel, such as tunable volatility of photonic color, broad range of color expression, low drive voltages, and easy fabrication, are promising for e-paper applications.

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