Light Induced Color Changes of Microgel-Based Etalons

*Yongfeng Gao, Michael J. Serpe**

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Abstract: Poly (*N*-isopropylacrylamide) (pNIPAm) microgel-based etalons were used to fabricate systems that change visual color in response to light exposure. These systems were fabricated by adding pH responsive microgel-based etalons to a solution composed of the photoacid *o*-nitrobenzaldehyde (*o*-NBA). Upon exposure of this system to ultraviolet (UV) irradiation, the photoacid released a proton, lowering the pH of the solution. Since the pNIPAm microgel-based etalon was responsive to pH, the etalon changed its optical properties, and hence visual color. We went on to show that patterned etalons could be fabricated, which only contained pH responsive microgels is specific regions. These etalons only changed color in the pH responsive regions, to yield patterns that change color upon UV light exposure. Finally, the etalon's color was shown to be fully reversible, and could be switched multiple times. These

unique systems could potentially be used for display technologies, and as a controlled/triggered drug delivery system.

Keywords: Stimuli responsive polymers, photoacids, microgel-based etalon, photonic materials, surface patterning, display technologies

Introduction

Photonic materials are composed of periodic arrays of contrasting refractive index materials, which interact with incident light (via reflection, refraction, and/or diffraction) to produce unique optical properties.[1-5] The refractive index periodicity can be in one, two, or three dimensions; while the specific optical properties depend on the spacing between the material's periodic elements and their refractive index. These materials often yield visually stimulating optical properties, but they also have numerous practical applications, such as photonic circuits,[6] optical filters,[7] and in communications.[8]

The most basic photonic materials are composed of elements with fixed positions and refractive indeces. While these "static" structures are of utmost importance, the tunability of the spacing and/or the refractive indeces of the photonic material's elements can make these devices even more useful.[9,10] Hence, the fabrication and development of materials and structures from components that are tunable has also been extensively studied.[9,11-13] These devices are very

unique due to their ability to change their optical properties (and color) in response to light,[14] electric field,[15] magnetic field,[16,17] temperature,[14,18,19] pH,[20] ionic strength,[21] solvent compositions, and humidity.[22,23] Among these, light is extremely useful due to its ability to address systems from remote locations; the extent of the response can be tuned by changing the excitation wavelength, intensity, and duration of excitation. Furthermore, the device can return to its initial state by simply removing the radiation source. Perhaps more interesting is the fact that certain wavelengths of light can also penetrate skin, allowing material transitions to be stimulated for controlled/triggered drug delivery. Specifically, certain waelengths of light that can penetrate skin can also lead to locatized heating; the heat generated can stimulate the device to release a small molecule drug.

Recently, we reported on polymer-based optical materials that exhibit unique optical properties and visual color, which can be tuned with temperature and other stimuli.[24-27] These devices were constructed by sandwiching a responsive polymer layer between two Au layers all supported on a glass substrate. This structure is akin to the mirror-dielectric-mirror structure of a classic Fabry–Perot etalon (etalon), see Figure 1. In this novel structure (shown in Figure 1a), the responsive polymer layer is composed of thermoresponsive poly (*N*-isopropylacrylamide) (pNIPAm)-based hydrogel particles (microgels). PNIPAm is well known to be water soluble at temperatures below 32 $^{\circ}$ C, becoming "insoluble" at higher temperatures.[28-30] As part of this transition, pNIPAm undergoes a random coil (extended) to a globule (collapsed) transition. Likewise, pNIPAm-based microgels undergo a swollen to collapsed transition as the temperature of the water they are in is increased to > 32 $^{\circ}$ C. The addition of comonomers into the microgels adds chemical functionality and can alter the microgel responsivity. Acid comonomers, such as acrylic acid (AAc),[24,29] adds pH responsivity to the already thermoresponsive microgels.

Specifically, the AAc monomer has a p*K*a of ≈ 4.25, so when pNIPAm-*co*-AAc microgels are exposed to a solution with a pH above the p*K*a for AAc the collapse transition is hindered. Furthermore, the microgels swell, which are both a result of Coulombic repulsion between the deprotonated AAc in the microgel. These effects are fully reversible by lowering the solution pH to below 4.25.

As indicated above, pNIPAm microgel-based etalons were constructed, which exhibit interesting optical properties, i.e., color and multipeak reflectance spectra (shown in Figure 1b). The position of the reflectance peaks can be predicted from Equation (1):[24,25]

$$\lambda m = 2nd \cos\theta \qquad (1)$$

where λ is the wavelength maximum of the peak (s), m is the peak order, n is the refractive index of the dielectric, d is the spacing between the mirrors, and θ is the angle of incidence. Therefore, since the microgel solvation state can be modulated with pH variations, and the microgels define the distance between the etalon's Au layers, the position of the reflectance peaks (and the etalon color) should depend on solution pH. That is, when the solution pH is above the p*K*a of AAc, the AAc groups become negatively charged, which results in microgel swelling and a concomitant increase in the distance between two Au layers. However, when the solution pH is again lowered to below AAc's p*K*a, the microgels decrease in diameter due to the AAc protonation; this results in a decrease in the distance between the etalon's Au layers. As can be predicted from equation 1, the increase and decrease in the distance between the Au layers results in a red shift and blue shift of the etalon's reflectance peaks, respectively.

Experimental Section

Materials: N -isopropylacrylamide was purchased from TCI (Portland, Oregon) and purified by recrystallization from hexanes (ACS reagent grade, EMD, Gibbstown, NJ) prior to use. N, N' – methylenebisacrylamide (99%), acrylic acid (99%), *o*-Nitrobenzaldehyde (*o*-NBA) and ammonium persufate (98+%) were obtained from Aldrich (St. Louis, MO) and were used as received. Polydimethylsiloxane (PDMS) (Sylgard 184) was purchased from Dow Corning Corporation and used as received. Anhydrous ethanol was obtained from Commercial Alcohols (Brampton, Ontario). All deionized water was 18.2 M Ω · cm and obtained from a Milli-Q Plus system from Millipore (Billerica, MA). Au annealing was performed in an Isotemp muffle furnace from Fisher Scientific (Ontario, Canada). Glass cover slides were 25 mm × 25 mm and obtained from Fisher Scientific. Cr (99.999%) was obtained from ESPI (Ashland, OR), while Au (99.99%) was obtained from MRCS Canada (Edmonton, AB). Photographs of the films were taken with a Canon Power shot SD20 Digital ELPH SD.

Microgel Synthesis: PNIPAm-*co*-AAc microgels were synthesized via free radical precipitation polymerization as described previously. The monomer mixture was comprised of 85% N -isopropylacrylamide (NIPAm) and 10% acrylic acid (AAc) with 5% N,N'-methylenebisacrylamide (BIS) cross linker. The monomer, NIPAm (11.9 mmol), and the cross linker, BIS (0.703 mmol), were dissolved in 18.2 M Ω · cm deionized water (99 mL) with stirring in a small beaker. The mixture was filtered through a 0.2 μm filter affixed to a 20 mL syringe into a 250 mL, 3-neck round bottom flask. The flask was then fitted with a temperature probe, a condenser/N_2 outlet, stir bar, and a N_2 inlet. The monomer solution was purged with N_2 gas for ≈ 1 hr with stirring, while the temperature was allowed to reach 70 °C. AAc (1.406 mmol) was added to the heated mixture with a micropipette. An aqueous solution of ammonium persulfate (APS; 0.046 g in 1.0 mL) was delivered to the monomer solution with a transfer

pipette to initiate the reaction, and reaction will continue for 4 h. Following completion of the reaction, the reaction mixture was filtered through glass wool to remove any large aggregates. The coagulum was rinsed with deionized water and the reaction solution was diluted to ≈ 120 mL. An aliquot of these particles (13 mL) in centrifuge tubes were centrifuged at a speed of ≈ 8500 relative centrifugal force (rcf) at 20 °C to produce a pellet. The supernatant was removed from the pellet of particles, which were then re-suspended to their original volume (13 mL) using deionized water. This process was completed a total of six times to remove the unreacted monomer and linear polymer from the microgels. For poly (N-isopropylacrylamide) microgels, the monomer mixture was comprised of 95% N -isopropylacrylamide (NIPAm) and 5% N,N'-methylenebisacrylamide (BIS) cross linker. The process is the same as above. The diameter of both the synthetic microgels are ~ 600 nm.

Etalon Fabrication: Etalon was prepared as previously described. To fabricate the Au coated coverslips (etalon underlayer), 2 nm Cr and 15 nm of Au was added to a 25 x 25 mm ethanol rinsed and N_2 gas dried glass coverslip (Fisher's Finest, Ottawa, ON) at a rate of 1 Å s-1, and 0.1 Å s-1, respectively (Torr International Inc., thermal evaporation system, Model THEUPG, New Windsor, NY). The Cr/Au substrates were annealed at 250 °C for 3 h (Thermolyne muffle furnace, Ottawa, ON) and cooled to room temperature prior to microgel film deposition. Approximately 5-10 mL of microgel solution was centrifuged at ~8300 rcf to form a pellet. The supernatant was removed and discarded, and the pellet was vortexed to loosen and homogenize the particles in the remaining solvent. A 40 uL aliquot of concentrated microgels were spread onto an annealed 25 mm x 25 mm Au-coated glass coverslip at 30 °C. The film was allowed to dry on a 35 °C hot plate for 120 minutes before the excess microgels were rinsed with deionized water. The samples were soaked overnight at 30 °C in a deionized water bath. The samples were

then rinsed with deionized water, dried with N_2, and another Au overlayer (2 nm Cr for adhesion, followed by 15 nm Au) was added. The completed device was soaked overnight in deionized water at 30 °C before spectral analysis.

Reflectance Spectroscopy: Reflectance measurements were conducted using a Red Tide USB650 spectrometer, a LS-1 tungsten light source, and a reflectance probe from Ocean Optics (Dunedin, FL). The spectra were record using Ocean Optics Spectra Suite Spectroscopy Software at room temperature over a wavelength range of 400-1000 nm. Measurements were conducted by placing the film in a Petri dish with water at room temperature. The probe tip was immersed in the water and its distance from the etalon surface adjusted for optimal signal. The probe remained undisturbed between measurements to ensure that all of the spectra were taken in the same manner. The UV irradiation was done by using a Blak-Ray® B-100AP High Intensity UV Lamp with wavelength in 365 nm.

Results and discussion

In this study, we developed a pNIPAm-*co*-AAc microgel-based etalon *system* that is capable of changing its optical properties and visual color in response to solution pH changes induced by UV light irradiation. To accomplish this we utilized the photoacid o-nitrobenzaldehyde (*o*-NBA); its structure and UV light-induced reaction is shown in Figure 2. The photoacid *o*-NBA was used because its behavior is well characterized and has been used in a variety of applications over a number of years.[31-34] As illustrated in Figure 2a, the molecule releases a proton under UV irradiation (UV Source: 365 nm longwave UV), which causes the solution pH to decrease.[35,36] To investigate the rate and efficiency of this process, we prepared aqueous solutions of various *o*-NBA concentrations (1 mM, 5 mM and 10 mM) and adjusted

their pH to ~7.00 by adding aliquots of 1 M NaOH solution. Each solution was continuously irradiated with UV light for the indicated time, while recording the solution pH every 10 sec. As can be seen in Figure 2b, when the solution concentration increases from 1 mM to 5 mM, the rate of pH change increases, while there is no change upon further increase of the solution concentration. Therefore, for subsequent experiments we chose to work with 5 mM *o*-NBA solutions. The pH of this solution was capable of a total pH change of ~3.6 pH units (pH 7.0 to 3.4). We also performed the same experiment in the absence of *o*-NBA, and found a negligible change in solution pH upon UV exposure.

With the ability to tune the pH of the *o*-NBA solution with UV irradiation, we determined if the optical properties of a pNIPAm-*co*-AAc microgel-based etalon could be tuned with UV irradiation. This is illustrated schematically in Figure 3. Initially, the pNIPAm-*co*-AAc microgel-based etalon was added to a Petri dish and 5 mM *o*-NBA solution (pH 7.00) was added. The etalon was allowed to incubate for ~60 min until the reflectance spectrum was stable, i.e., there was no observable change in the position of the reflectance peaks for at least 30 min. Since the initial solution pH was greater than the microgel's p*K*a, the microgels were swollen and the mirrors were relatively far apart. Exposure of the system to the UV light caused the solution pH to decrease, as shown in supporting information (ESI), resulting in a spectral shift from the etalon as can be seen in Figure 4. As can be seen, exposing the system to UV light for 10 sec, followed by stabilization in the absence of UV light caused the solution pH to decrease by approximately 2 units resulting in a blue shift in the position of the reflectance peak. This is expected since the microgel's AAc groups were protonated. Furthermore, the system was again exposed to UV light for 10 sec, followed by stabilization in the absence of UV light exposure. The solution pH subsequently dropped again, resulting in a spectral blue shift. As can be seen,

the total wavelength shift was 160 nm. From this large spectral shift, we hypothesized that this system could be used to visually change the color of the etalons.

To investigate this, we constructed an etalon with a specific region masked off with poly(dimethylsiloxane) (PDMS, Sylgard 184). The PDMS mask was cut in such a way as to cover part of the etalon, while exposing the rest. In this case, we cut the PDMS mask to expose the etalon such that the letters “UA” are formed. To accomplish this, the prepared PDMS mask (see Experimental section) was added to the top of the etalon and sealed by applying pressure. This assembly was subsequently exposed to a 5 mM *o*-NBA solution with a pH close to 7. The unmasked "UA" region was in direct contact with the solution, while the masked region remained unexposed. After soaking for several minutes, the system was exposed to UV light for 60 sec to trigger the solution pH change, which lead to a dramatic color change in the patterned, exposed region. As can be seen in Figure 5, the protected region was covered with PDMS and remained blue, while the region exposed to the solution was initially red, which changed to green upon ~1 min UV exposure and wait for few mins to stable. This is clearly depicted in the UA patterned region of the photograph. What is interesting is the initial color of the patterned region could be regenerated by replenishing the *o*-NBA. Furthermore, the color of the patterned region could be switched again by exposure to UV light. This color change can be repeated over many cycles with great fidelity and reproducibility, as can be seen in Figure 6. We also determined that further exposure of the system to UV irradiation, past the 60 sec exposure, has no effect on the pH, and hence no effect on the etalon's color. This can be seen in the electronic supporting information (ESI).

Finally, we patterned a single substrate such that a defined region contained pH responsive microgels, while other regions contained non-pH responsive microgels. Specifically,

we synthesized pNIPAm-based microgels with and without AAc, such that they were both approximately the same diameter (~600 nm). Using a PDMS mask, part of the etalon was covered and non-pH responsive pNIPAm microgels painted in the uncovered region -- in this case, the mask was in the shape of a maple leaf. Following this step, the mask was removed and the the microgels allowed to dry, and were rinsed following our defined protocol to yield a monolayer of microgel in that region.[24] Then, the rest of the substrate (the maple leaf region) was painted with pNIPAm-*co*-AAc microgels. Again, our previously described protocol was used to yield a single microgel layer in that region.[24] Following the coating of the respective regions of the substrate with microgels, the whole substrate was covered with a thin layer of Au to yield an etalon. The complete process is shown in ESI. As can be seen in Figure 7, after soaking the device in the 5 mM *o*-NBA solution with pH ~7, the different regions appeared similar in color, showing the uniformity of the patterned regions. The system was then exposed to UV irradiation, and a photograph of the device taken every one minute. As can be seen in Figure 7, the device clearly changes color in the region where the pNIPAm-*co*-AAc were painted, while the region containing the pNIPAm microgels remained unchanged. Again, the region containing the pNIPAm-*co*-AAc microgels is reacting to the UV-induced solution pH changes, changing the distance between the etalon's Au layers, while the pNIPAm microgels remain unresponsive to the solution pH changes. The maple leaf color change also can be repeated by immersing the etalon into a fresh *o*-NBA solution and re-exposure to UV light, as shown in ESI.

In conclusion, we show that UV light could be used to decrease the pH of an aqueous solution containing *o*-NBA. This is a direct result of the UV light inducing the *o*-NBA to release a proton. Furthermore, by immersing a pNIPAm-*co*-AAc microgel-based etalon in this solution, we were able to tune its optical properties upon UV irradiation. This was a direct result of the

pNIPAm-*co*-AAc microgels changing solvation state in response to the solution pH changes, which directly alters the optical properties of the etalon. We were able to fabricate patterned etalons, and change the visual color in those specific regions. Finally, the optical properties of the devices were reversible by simply adding fresh *o*-NBA solution and reexposing the device to UV light. These unique properties will be expoited in the future for display technologies, and controlled/triggered drug delivery.

Figures

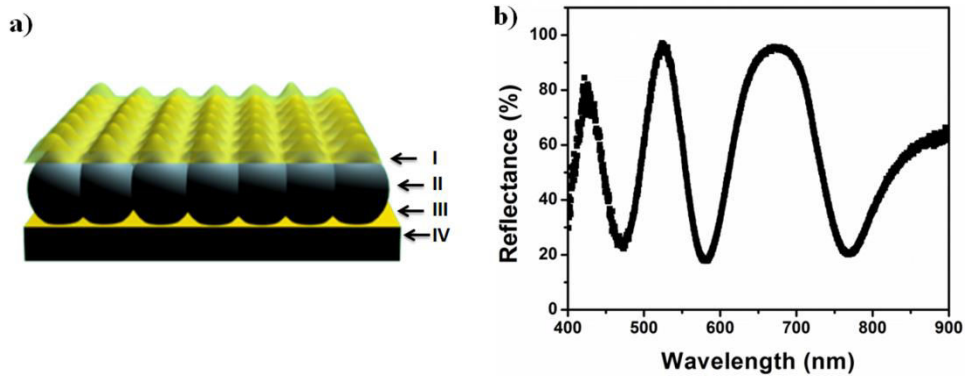


Figure 1. a) The structure of a standard microgel-based etalon composed of (I and III) two Au layers sandwiching a (II) microgel layer, all on a (IV) glass support. b) typical reflectance spectrum obtained from a microgel-based etalon immersed in deionized water.

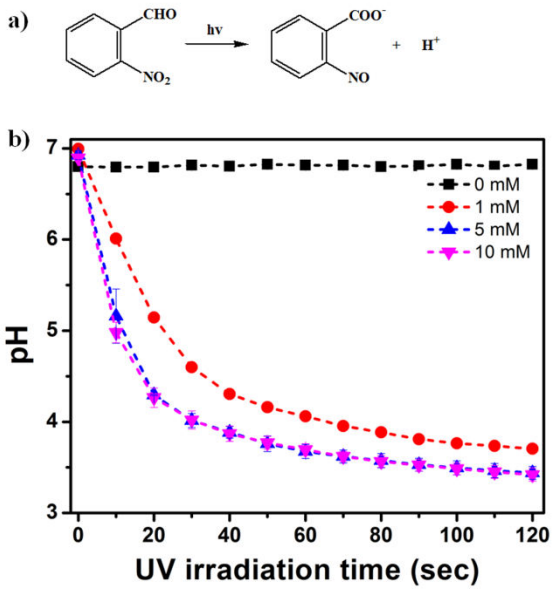


Figure 2. a) The reaction of *o*-NBA induced by exposure to UV irradiation and b) the observed change in solution pH after exposure of aqueous solution of the indicated *o*-NBA concentrations to UV irradiation for the indicated elapsed times.

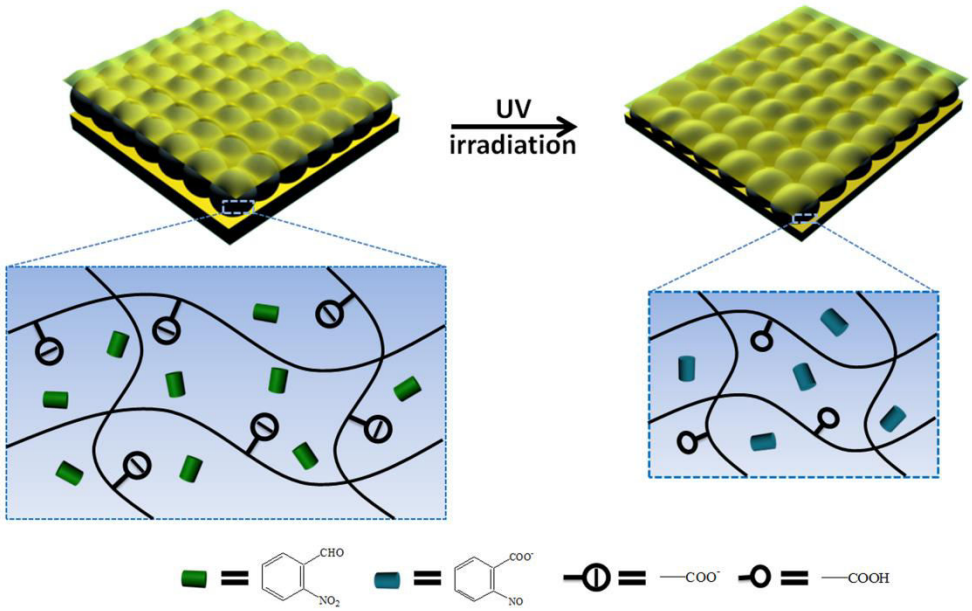


Figure 3. Schematic illustration of the reaction of the pNIPAm microgel-based etalon system upon exposure to UV irradiation. Upon UV exposure, the *o*-NBA produces a proton, which lowers the pH of the solution. The decrease in solution pH results in protonation of the pNIPAm-*co*-AAc microgels, which alters their solvation state and the optical properties of the etalon.

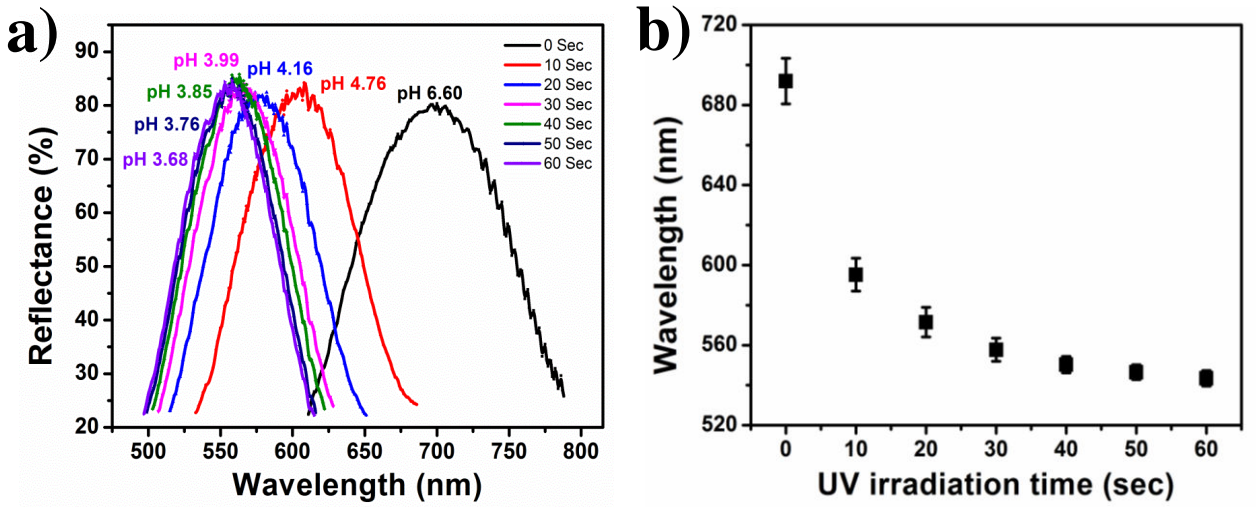


Figure 4. a) Reflectance spectrum for a device in *o*-NBA solution after exposure to UV irradiation for the indicated times. For these experiments, the device was initially stabilized in a *o*-NBA solution (5 mM) of pH 6.60, then exposed to UV irradiation for the indicated times (total irradiation times). After exposure to UV irradiation for the indicated times, the UV light was removed and the etalon allowed to stabilize. b) The final peak positions as a function of total irradiation time. Each point is the average obtained by analyzing 3 separate etalons and the error bars indicate the standard deviation.

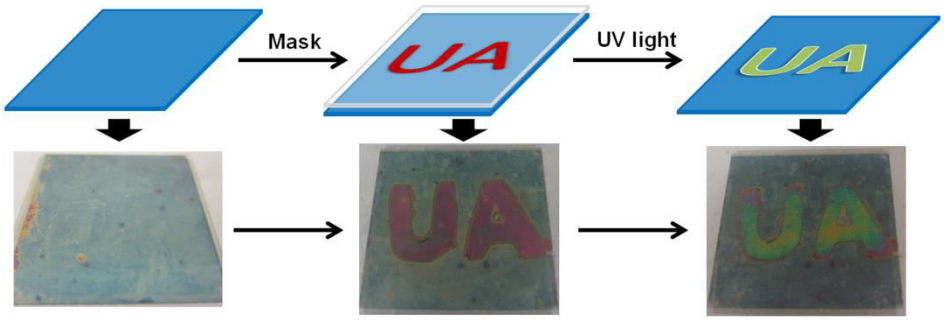


Figure 5. The color change of an etalon exposed to *o*-NBA solution (5 mM) only in a specific region, which was defined by a PDMS mask. Upon UV exposure, the color of the device visually changes.

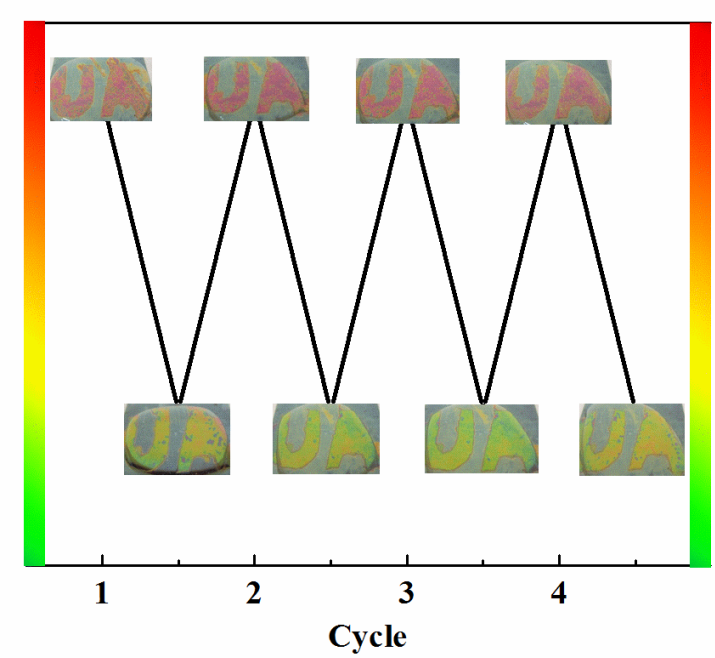


Figure 6. The reversibility of the etalon's color by repeated exposure to UV irradiation followed by the addition of fresh *o*-NBA solution.

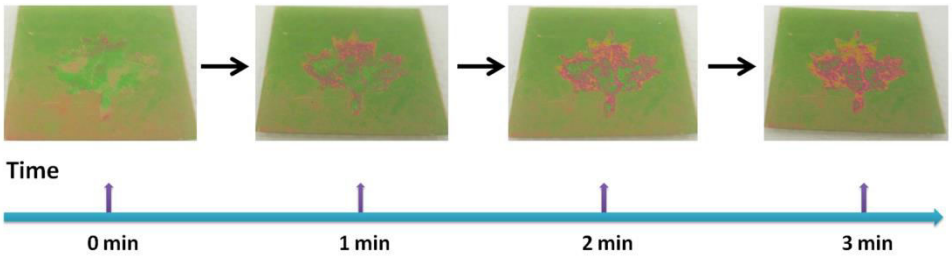
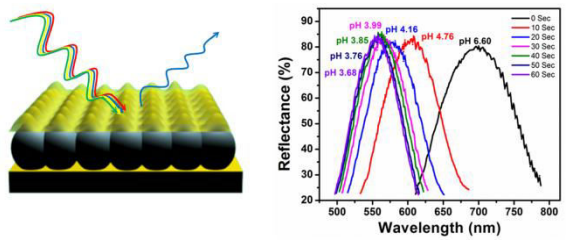


Figure 7. The response of a patterned etalon immersed in o-NBA solution (5 mM) after exposure to UV irradiation for the indicated times. In this case, the maple leaf region was composed of pH

responsive pNIPAm-co-AAc microgels, while the rest of the device was composed of non-pH responsive pNIPAm microgels.

The table of contents



AUTHOR INFORMATION

Corresponding Author

*E-mail: michael.serpe@ualberta.ca.

ACKNOWLEDGMENT

MJS acknowledges funding from the University of Alberta (the Department of Chemistry and the Faculty of Science), the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canada Foundation for Innovation (CFI), the Alberta Advanced Education & Technology Small Equipment Grants Program (AET/SEGP) and Grand Challenges Canada. MJS acknowledges Mark McDermott for the use of the thermal evaporator.

ASSOCIATED CONTENT

Supporting Information. The pH profile with as a function of time for 10 s UV exposures. Photographs of etalons illustrating the stability of their color after UV irradiation. The procedure used for patterning etalons. The repeatability of the color change for a patterned etalon. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES

(1) Ozin, G. A.; Yang, S. The Race for the Photonic Chip: Colloidal Crystal Assembly in Silicon Wafers. *Adv. Funct. Mater.* **2001**, *11*, 95-104.

(2) Wijnhoven, J. E.; Vos, W. L. Preparation of Photonic Crystals Made of Air Spheres in Titania. *Science* **1998**, *281*, 802-804.

(3) Braun, P. V.; Wiltzius, P. Microporous Materials: Electrochemically Grown Photonic Crystals. *Nature* **1999**, *402*, 603-604.

(4) Jiang, P.; Bertone, J. F.; Colvin, V. L. A Lost-Wax Approach to Monodisperse Colloids and Their Crystals. *Science* **2001**, *291*, 453-457.

(5) Colvin, V. L. From Opals to Optics: Colloidal Photonic Crystals. *Mrs Bulletin* **2001**, *26*, 637-641.

(6) Pauzauskie, P. J.; Yang, P. Nanowire Photonics. *Mater.Today* **2006**, *9*, 36-45.

(7) Lin, S.-y.; Fleming, J.; Hetherington, D.; Smith, B.; Biswas, R.; Ho, K.; Sigalas, M.; Zubrzycki, W.; Kurtz, S.; Bur, J. A Three-Dimensional Photonic Crystal Operating at Infrared Wavelengths. *Nature* **1998**, *394*, 251-253.

(8) Deubel, M.; Von Freymann, G.; Wegener, M.; Pereira, S.; Busch, K.; Soukoulis, C. M. Direct Laser Writing of Three-Dimensional Photonic-Crystal Templates for Telecommunications. *Nat. Mater.* **2004**, *3*, 444-447.

(9) Aguirre, C. I.; Reguera, E.; Stein, A. Tunable Colors in Opals and Inverse Opal Photonic Crystals. *Adv. Funct. Mater.* **2010**, *20*, 2565-2578.

(10) Parker, A. R.; Townley, H. E. Biomimetics of Photonic Nanostructures. *Nat. Nanotechnol.* **2007**, *2*, 347-353.

(11) Arsenault, A. C.; Puzzo, D. P.; Manners, I.; Ozin, G. A. Photonic-Crystal Full-Colour Displays. *Nature Photon.* **2007**, *1*, 468-472.

(12) Debord, J. D.; Eustis, S.; Byul Debord, S.; Lofye, M. T.; Lyon, L. A. Color‐Tunable Colloidal Crystals from Soft Hydrogel Nanoparticles. *Adv. Mater.* **2002**, *14*, 658-662.

(13) Sato, O.; Kubo, S.; Gu, Z.-Z. Structural Color Films with Lotus Effects, Superhydrophilicity, and Tunable Stop-Bands. *Acc.Chem. Res.* **2008**, *42*, 1-10.

(14) Garcia, A.; Marquez, M.; Cai, T.; Rosario, R.; Hu, Z.; Gust, D.; Hayes, M.; Vail, S. A.; Park, C.-D. Photo-, Thermally, and pH-Responsive Microgels. *Langmuir* **2007**, *23*, 224-229.

(15) White, T. J.; McConney, M. E.; Bunning, T. J. Dynamic Color in Stimuli-Responsive Cholesteric Liquid Crystals. *J. Mater. Chem.* **2010**, *20*, 9832-9847.

(16) Ge, J.; Yin, Y. Magnetically Tunable Colloidal Photonic Structures in Alkanol Solutions. *Adv. Mater.* **2008**, *20*, 3485-3491.

(17) Ge, J.; Yin, Y. Magnetically Responsive Colloidal Photonic Crystals. *J. Mater. Chem.* **2008**, *18*, 5041-5045.

(18) Holtz, J. H.; Asher, S. A. Polymerized Colloidal Crystal Hydrogel Films as Intelligent Chemical Sensing Materials. *Nature* **1997**, *389*, 829-832.

(19) Debord, J. D.; Lyon, L. A. Thermoresponsive Photonic Crystals. *J. Phy. Chem. B* **2000**, *104*, 6327-6331.

(20) Yue, Y. F.; Haque, M. A.; Kurokawa, T.; Nakajima, T.; Gong, J. P. Lamellar Hydrogels with High Toughness and Ternary Tunable Photonic Stop‐Band. *Adv. Mater.* **2013**. *25*, 3106-3110

(21) Lee, K.; Asher, S. A. Photonic Crystal Chemical Sensors: pH and Ionic Strength. *J. Am. Chem. Soc.* **2000**, *122*, 9534-9537.

(22) Wang, Z.; Zhang, J.; Xie, J.; Li, C.; Li, Y.; Liang, S.; Tian, Z.; Wang, T.; Zhang, H.; Li, H. Bioinspired Water‐Vapor‐Responsive Organic/Inorganic Hybrid One‐Dimensional Photonic Crystals with Tunable Full‐Color Stop Band. *Adv. Funct. Mater.* **2010**, *20*, 3784-3790.

(23) Huang, J.; Tao, C.-a.; An, Q.; Lin, C.; Li, X.; Xu, D.; Wu, Y.; Li, X.; Shen, D.; Li, G. Visual Indication of Enviromental Humidity by Using Poly (Ionic Liquid) Photonic Crystals. *Chem. Commun.* **2010**, *46*, 4103-4105.

(24) Sorrell, C. D.; Carter, M. C.; Serpe, M. J. Color Tunable Poly (N‐Isopropylacrylamide)‐co‐Acrylic Acid Microgel‐Au Hybrid Assemblies. *Adv. Funct. Mater.* **2011**, *21*, 425-433.

(25) Sorrell, C. D.; Serpe, M. J. Reflection Order Selectivity of Color‐Tunable Poly (N‐isopropylacrylamide) Microgel Based Etalons. *Adv. Mater.* **2011**, *23*, 4088-4092.

(26) Hu, L.; Serpe, M. J. Color Modulation of Spatially Isolated Regions on a Single Poly (N-isopropylacrylamide) Microgel Based Etalon. *J. Mater. Chem.* **2012**, *22*, 8199-8202.

(27) Hu, L.; Serpe, M. J. Color-Tunable Etalons Assembled from Poly (N-isopropylacrylamide) Based Microgels. *Polymers* **2012**, *4*, 134-149.

(28) Wu, C.; Zhou, S. Laser Light Scattering Study of the Phase Transition of Poly (N-isopropylacrylamide) in Water. 1. Single Chain. *Macromolecules* **1995**, *28*, 8381-8387.

(29) Debord, J. D.; Lyon, L. A. Synthesis and Characterization of pH-Responsive Copolymer Microgels with Tunable Volume Phase Transition Temperatures. *Langmuir* **2003**, *19*, 7662-7664.

(30) Pelton, R.; Chibante, P. Preparation of Aqueous Latices with N-Isopropylacrylamide. *Colloids Surf.* **1986**, *20*, 247-256.

(31) Zhao, H.; Sterner, E. S.; Coughlin, E. B.; Theato, P. O-Nitrobenzyl Alcohol Derivatives: Opportunities in Polymer and Materials Science. *Macromolecules* **2012**, *45*, 1723-1736.

(32) Zhao, B.; Moore, J. S.; Beebe, D. J. Surface-Directed Liquid Flow Inside Microchannels. *Science* **2001**, *291*, 1023-1026.

(33) Cabane, E.; Malinova, V.; Meier, W. Synthesis of Photocleavable Amphiphilic Block Copolymers: Toward the Design of Photosensitive Nanocarriers. *Macromolecular chemistry and physics* **2010**, *211*, 1847-1856.

(34) DeMuth, P. C.; Min, Y.; Huang, B.; Kramer, J. A.; Miller, A. D.; Barouch, D. H.; Hammond, P. T.; Irvine, D. J. Polymer Multilayer Tattooing for Enhanced DNA Vaccination. *Nat. Mater.* **2013**, *12*, 367-376.

(35) Ciamician, G.; Silber, P. Chemische Lichtwirkungen. *Ber. deuts. chem. Ges.* **1901**, *34*, 1530-1543.

(36) Donten, M. L.; Hamm, P.; VandeVondele, J. A Consistent Picture of the Proton Release Mechanism of o NBA in Water by Ultrafast Spectroscopy and Ab Initio Molecular Dynamics. *J. Phy. Chem. B* **2011**, *115*, 1075-1083.