Ultrahigh-water-content photonic hydrogels with large electro-optic responses in visible to near-infrared region

Youfeng Yue [a,b,c] *, Yasuo Norikane [a], Jian Ping Gong [d]

[a]Research Institute for Advanced Electronics and Photonics, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, 305-8565, Japan.

[b]PRESTO, Japan Science and Technology Agency, Kawaguchi 332-0012, Japan.

[c]Graduate School of Life Science, Hokkaido University, Sapporo 001-0021, Japan.

[d]Faculty of Advanced Life Science, Institute for Chemical Reaction Design and Discovery, Soft Matter GI-CoRE, Hokkaido University, Sapporo, Hokkaido, 001-0021, Japan.

E-mail: yue-yf@aist.go.jp

Experimental section

1.1 Materials

Dodecyl glyceryl itaconate (DGI: n-C12H25-OCOCH2C(=CH2)COOCH2CH(OH) CH2OH) was synthesized according to the procedure described by Tsuji et al.[1] The product was purified on a silica gel column and eluted with hexane/ethyl acetate mixture (1:1 by volume). The collected DGI product was further purified by recrystallization in acetone/hexane mixture (1/1 by weight). Other chemicals (such as N, N'-methylenebis(acrylamide), acrylamide, sodium dodecyl sulfate, NaOH) are commercially available, which are mainly purchased from Aldrich and Wako Co., Japan.

1.2 Characterizations

Water content of the hydrogel, q, was calculated according to $q=(m_1-m_0)/m_1$, where m_1 and m_0 are the mass of the gel in the wet and dried states, respectively. The dried sample was measured by keeping it in an oven to achieve a constant dried state. Stress/relaxation tests were performed at room temperature by loading-unloading with a predefined strain of 80% on a commercial tensile machine (EZ-LX, SHIMATSU). The samples were cut into a dumbbell shape by a mould (JIS K-6251-7, DUMBBELL Co. LTD) with gauge length of 12 mm and width of 2 mm. The thickness of the samples was measured before test with a micrometer. All the stretch rate of loading and unloading was kept at 30 mm/min. Small-angle X-ray scattering measurements were carried out with a Rigaku NANO-Viewer with Cu-Ka radiation (40 kV and 30 mA, λ=0.154 nm, camera length=680mm). The electric field was supplied by a switching mode power DPS 3003

(CUSTOM), and the aluminium films were used as electrodes. The reflection spectrum was measured on Hamamatsu (C10027A10687, C10027) and Jasco V-550 Spectrophotometer with an incident and reflection angles of 60°. The surface three-dimensional height maps of the electrically patterned regions were characterized using laser scanning confocal microscopy (VK-X150, KEYENCE, Japan).

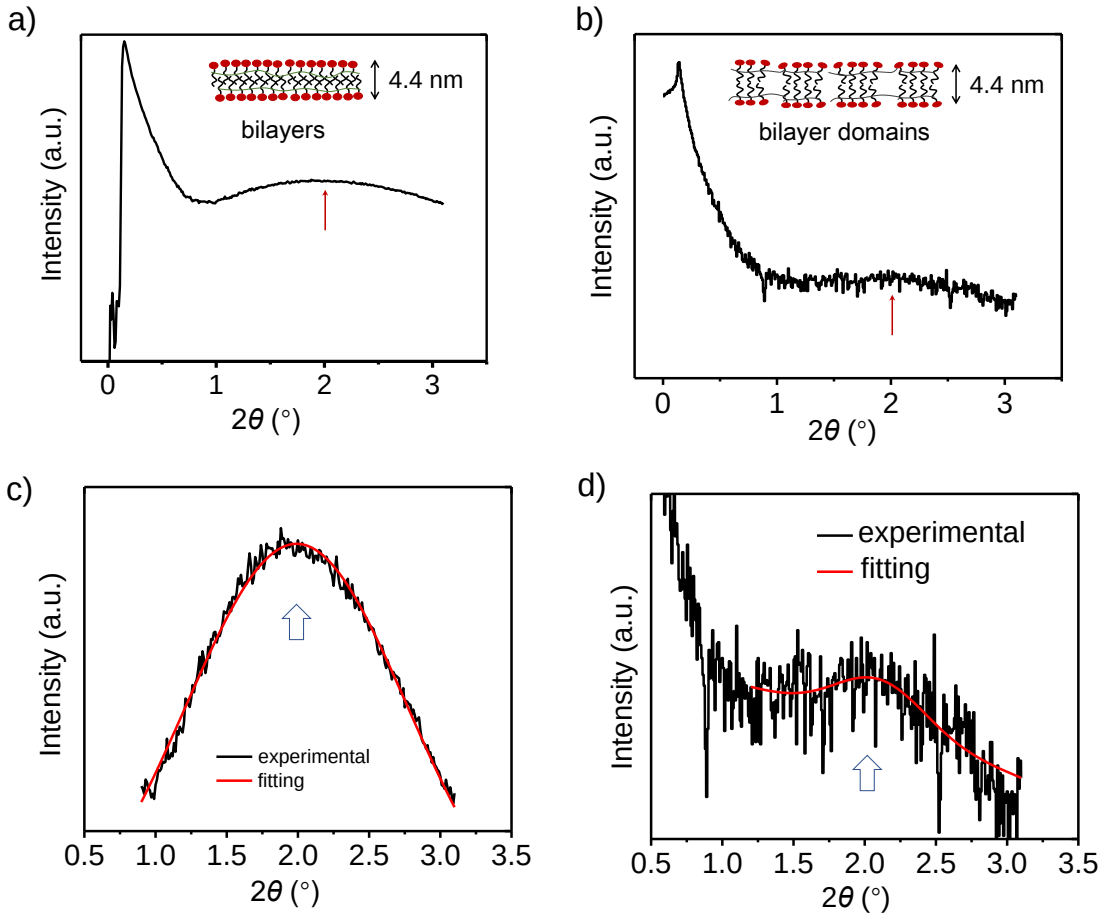

Figure S1 (a,b) 1D SAXS intensity for the samples before and after chemical treatment. Schematics of bilayer and bilayer domains were inserted in the top. (c, d) 1D SAXS and fitting data. Both broad peaks before (a) and after treatment (b) were appeared at 2θ=2°, corresponding to thickness of ~4.4 nm that calculated from the equation $2d\sin\theta=0.154$ (CuKα transition photons of wavelength λ=0.154 nm). The X-ray beam was imposed parallel to the lamellar plane.

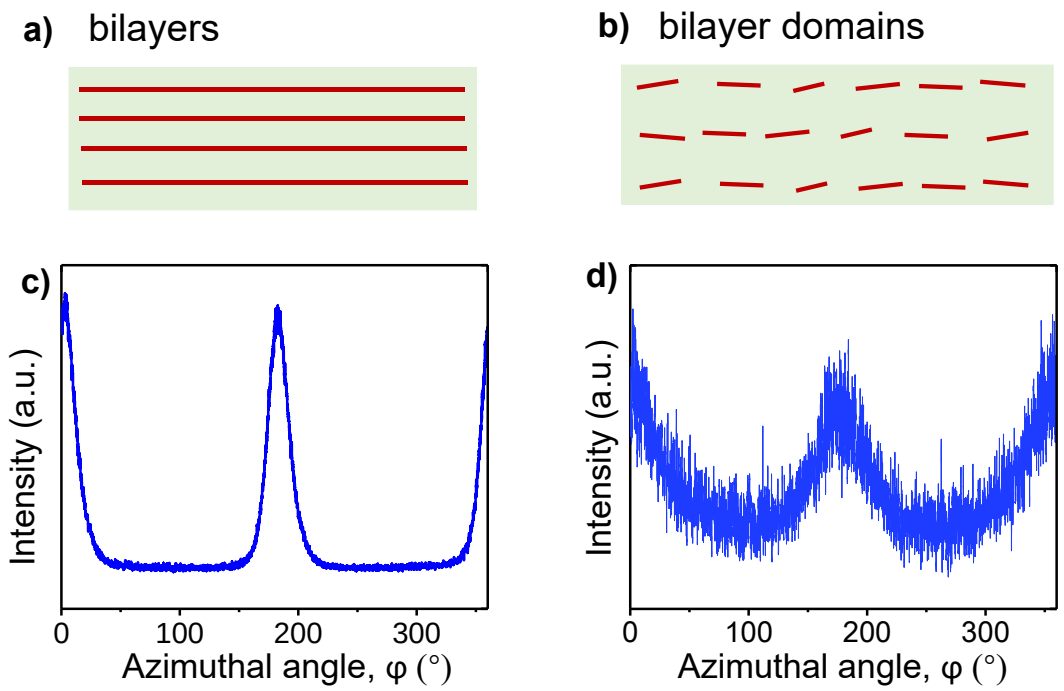

Figure S2 (a, b) Schematics of bilayers (red) and bilayer domains (red) in the polyelectrolyte hydrogels (light-green). (c, d) Azimuthal dependence of scattering intensity for the sample with bilayers (c) and bilayer domain structure (d).

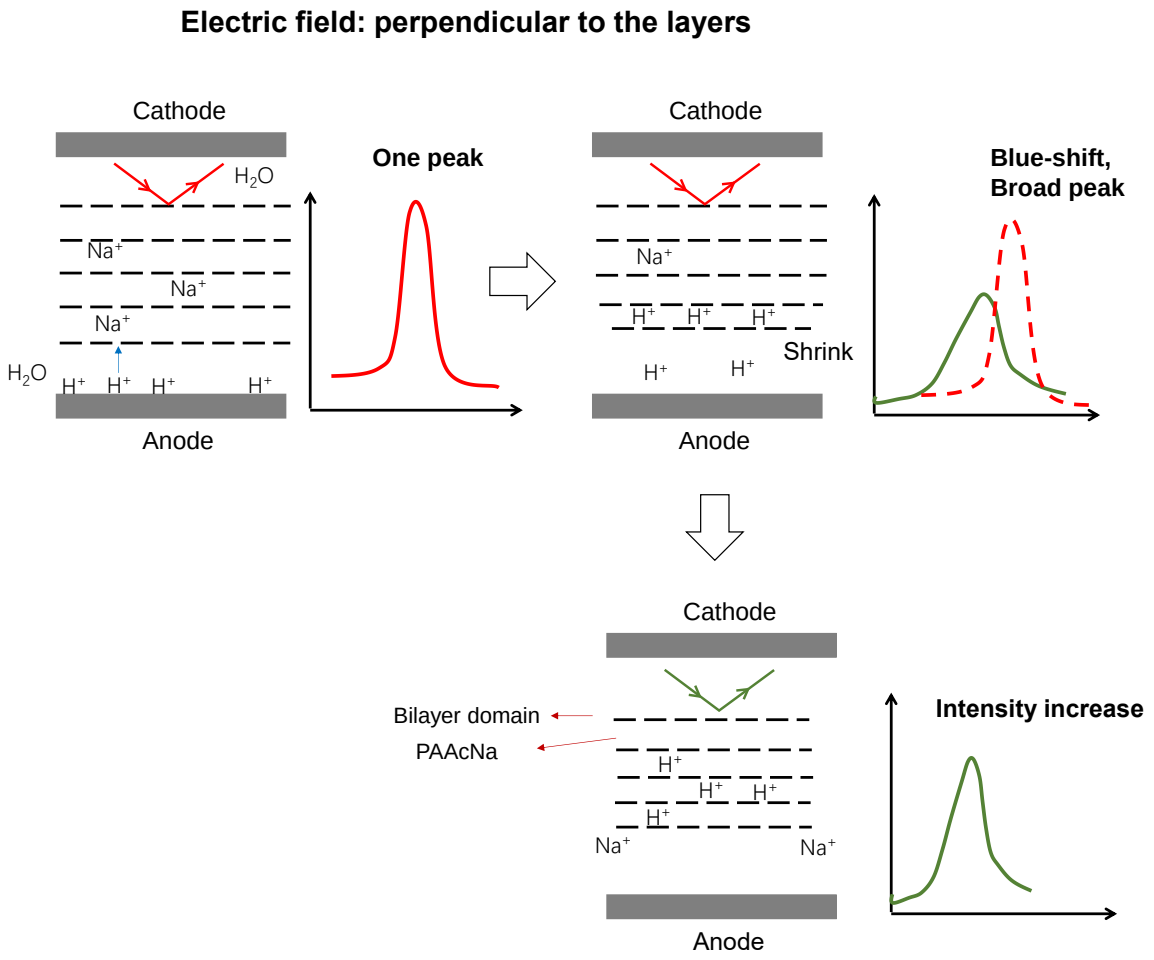

Figure S3 The schemtaic illustrations of the structure change and their corresponding reflectron spectrum change with time upon electric filed perpendicular to the layers.

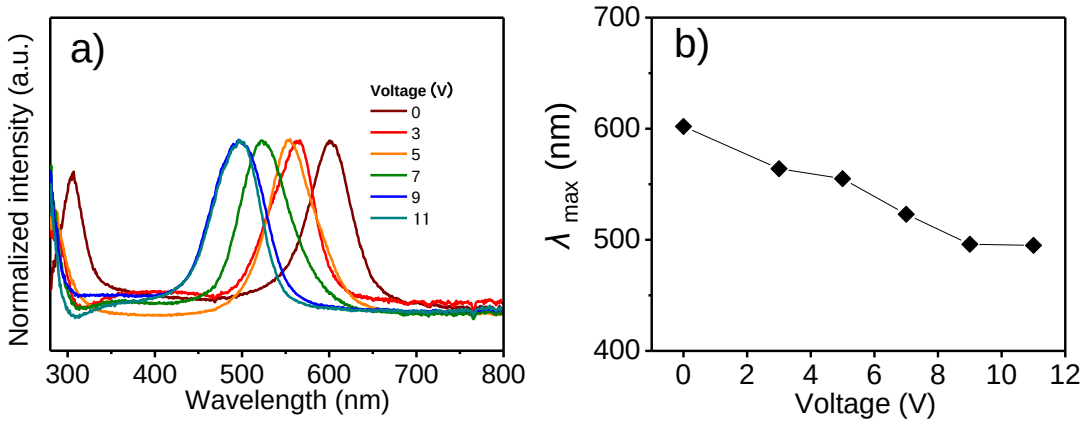

Figure S4 Refelction spectrum (a) and the maximum wavelength (b) with increasing in voltage values upon an electric field perpendicular to layers.

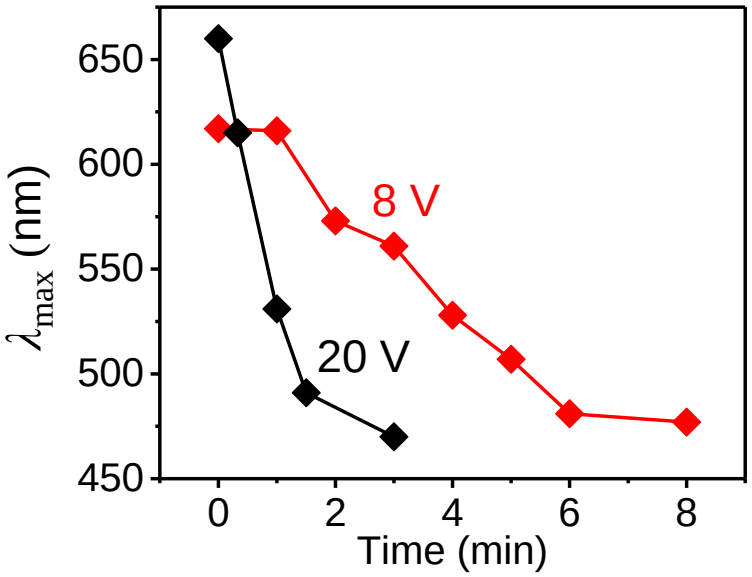

Figure S5 The electro-optic response speed of the hydrogel increased by using a high volatge in the direction perpendicular to layers.

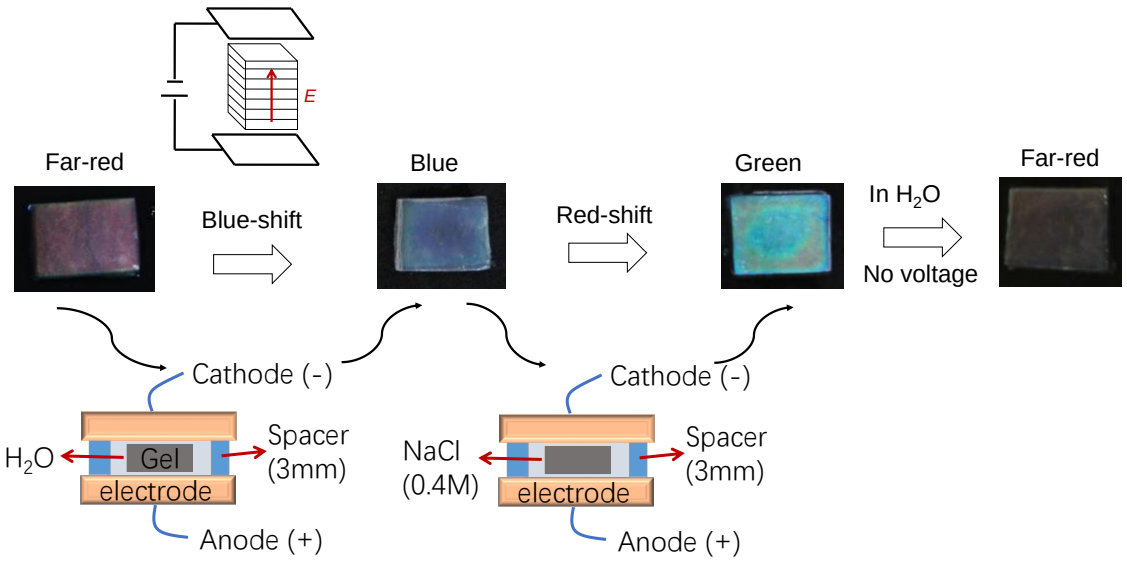

Figure S6 The electric-optic responses in the layered photonic hydrogel upon an electric field perpendicular to the layers. When the filled sollution was water, the hydrogel exhibited a blue-shift in the structural upon an perpendicular electric filed. When the filled solution changed to NaCl solution (0.4 M), the hydrogel showed a red shift. Please note that this gel exhibited blue shift in NaCl solution (0.4 M) without electric field due to the high ionic strenth. The recovery in the structural color was achieved by immersing the gel in water for 4 h. The experiments were performed on the same sample continuously.

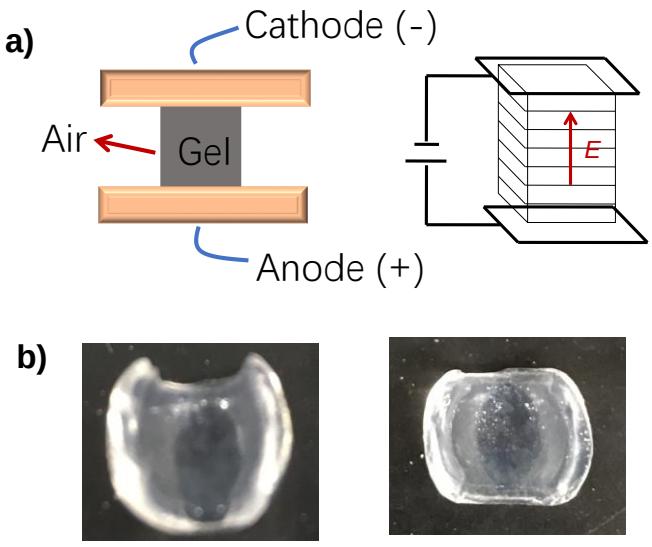

Figure S7 An electric field (*E*) applied in the direction perpendicular to the gel layers. The sample was directly in contact to the two electrodes (with no water surrounding). The tested sample bended to the anode side significantly due to the anisotropic swelling.

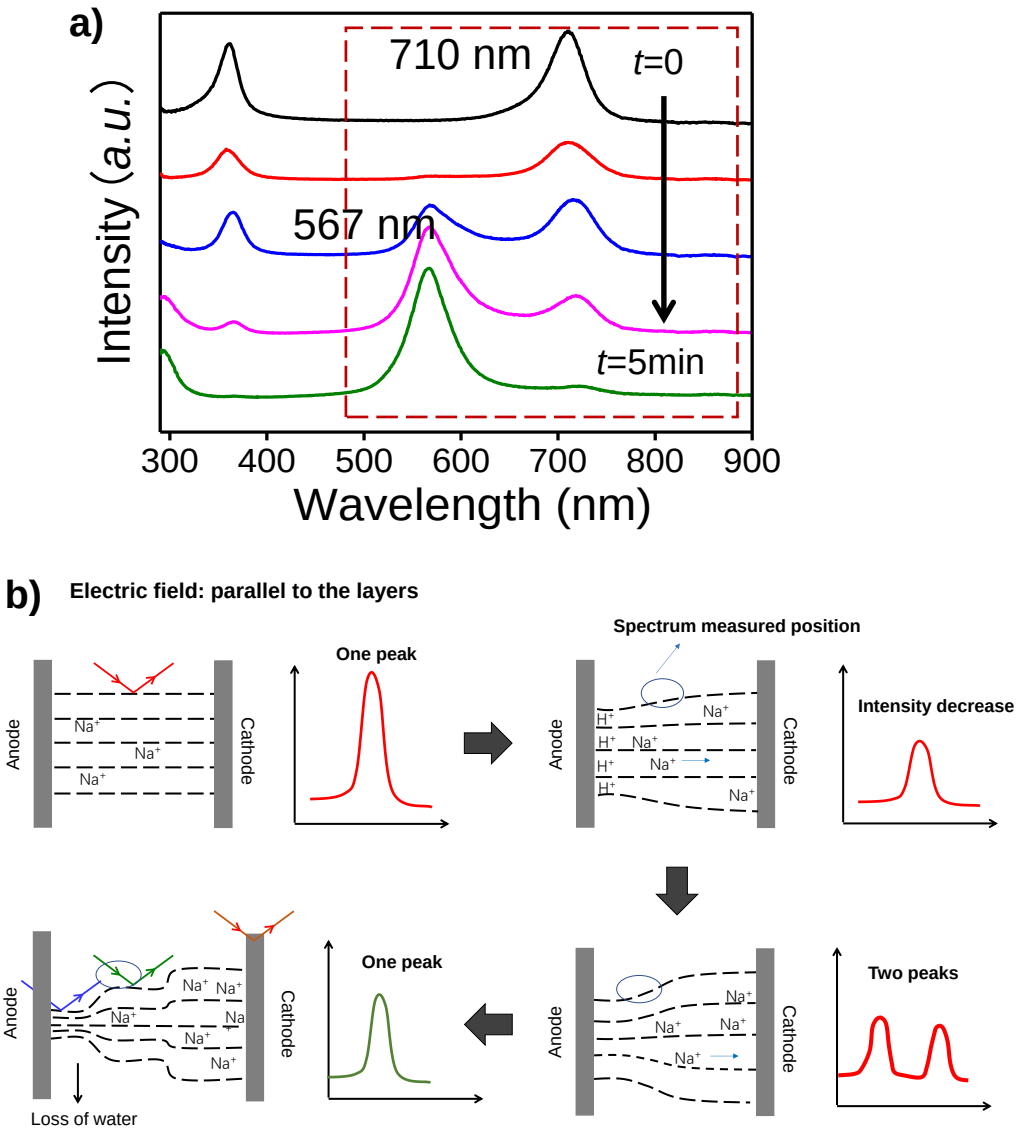

Figure S8 (a) The change of the reflection spectrum with time during appliying electric field parallel to the layers. (b) The schematic illustration of layered structure change and their corresponding reflectron spectrum change with time upon electric filed parallel to layers.

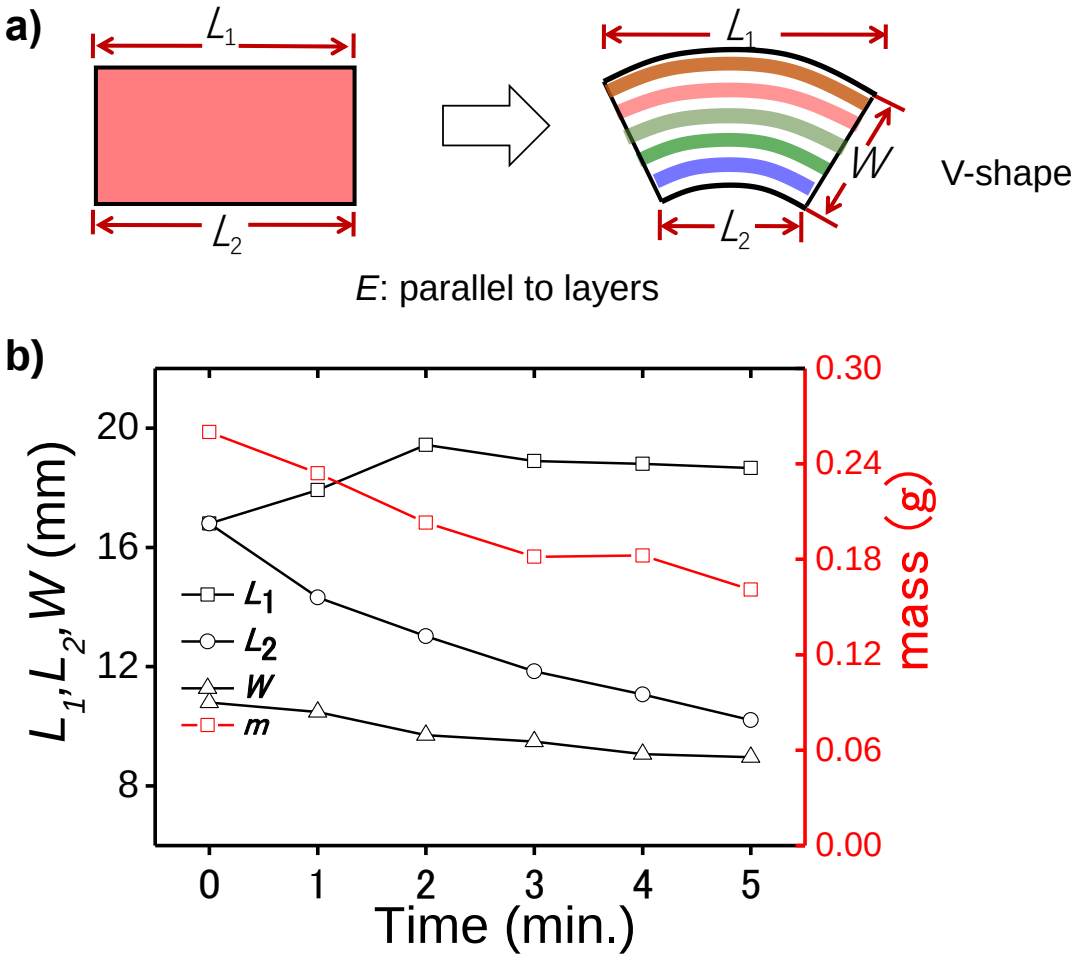

Figure S9 (a) Schematics of shape change of the layered hydrogel upon electric field parallel to the layers. (b) Size and mass change of the hydrogel with time upon electric field parallel to the layers.

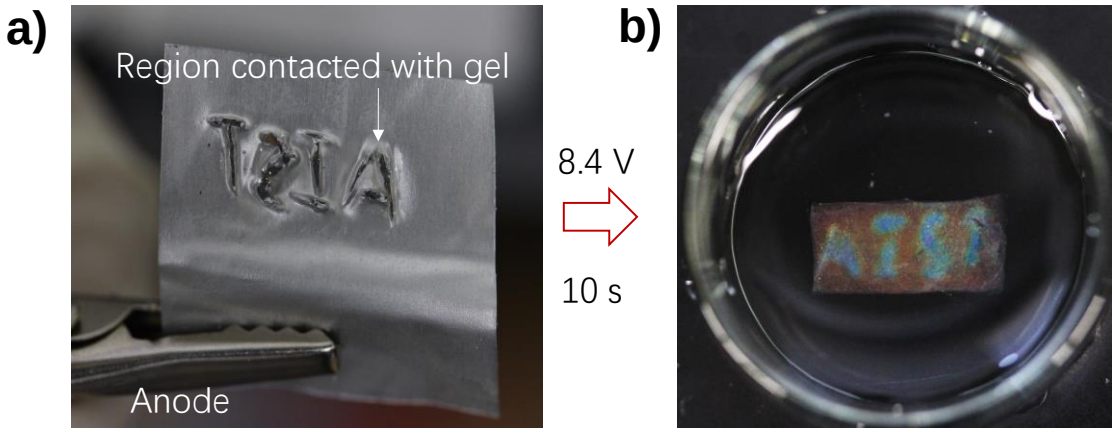

Figure S10 (a) The patterned electrode can be simply made by hand using a conductive aluminium film. For example, the characters "AIST" was cut with knife and transferred to the photonic hydrogel. After actuated with a voltage, the characters appeared on the gel in water even after removing the electrical stimuli (b).

There are many soft photonic crystals/hydrogels (including this hydrogel) show mechanical-induced color change/patterns upon stress.[2] However, the mechanical-induced color change or patterns disappeared immediately after removing the stress (stimuli). These electric-induced patterns can keep in water for long time and gradually reversable to initial state, which is one of the characters that different with other systems. Also, there are some demonstrations of producing permanent patterns on photonic crystals by other technologies, such as laser engraving or inkjet printing.[3-4] However, these patterns are generally irreversible once after produced.

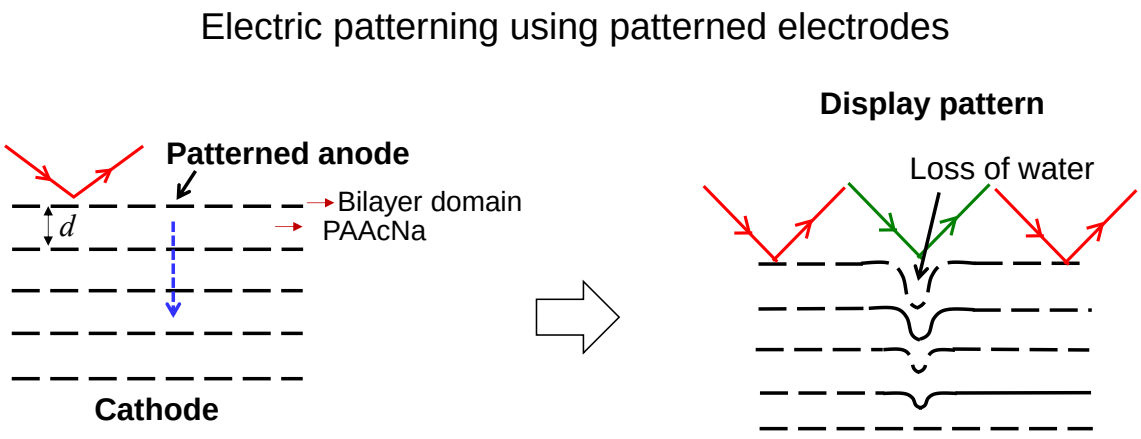

Figure S11 The electric patterning was achieved with a patterned electrode upon applying electric field in the direction perpendicular to the layers. The voltage applied regions exhibit shrinking and blue shift in color.

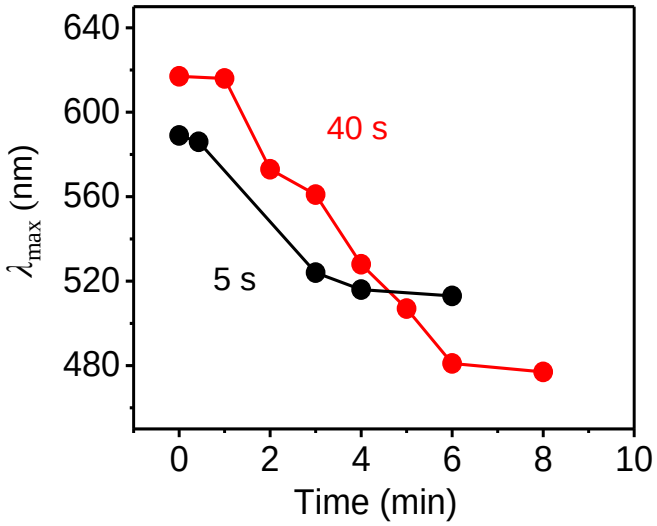

Figure S12 The electro-optic responses of the hydrogels with different NaOH treatment time.

Supplementary Movie 1

A move showing that the photonic hydrogel after chemical treatment absorbed water and swelled largely with a structural color change from blue to far-red. The size of the hydrogel after swelling was about 1.6 times of the original size. (Speed x16)

Supplementary Movie 2

A movie showing that the electric-induced pattern (a character of A) was displayed on the hydrogel in water.

References

[1] K. Naitoh, Y. Ishii, K. Tsujii, *J. Phys. Chem.* **1991**, *95*, 7915.

[2] Y. Yue, T. Kurokawa, M. A. Haque, T. Nakajima, T. Nonoyama, X. Li, I. Kajiwara, J. P. Gong, *Nat. Commun.* **2014**, *5*, 4659.

[3] Y. Yue, T. Kurokawa, *ACS Appl. Mater. Interfaces* **2019**, *11*, 10841.

[4] L. Cui, Y. Li, J. Wang, E. Tian, X. Zhang, Y. Zhang, Y. Song, L. Jiang, *J. Mater. Chem.* **2009**, *19*, 5499.