Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Electrophoretic Fabrication of Active and Selective Wrinkle Surface on Hydrogel

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Materials.

N,N-Dimethylacrylamide (DMAAm) and *N*-isopropylacrylamide (NIPAAm) were purchased from FUJIFILM Wako Pure Chemical Corporation and used after distillation and recrystallization, respectively. Methylenebisacrylamide (MBAAm) were purchased from FUJIFILM Wako Pure Chemical Corporation and used as purchased without further purification. Sodium poly(4-styrenesulfonate) (PSS), 4-stylenesulfonic acid sodium salt (SSNa), and fluorescein-*o*-acrylate were purchased from Aldrich and used as purchased without further purification. Poly(diallyldimethylammonium chloride) (PDDA) was purchased from Aldrich as aqueous solution and used after freeze dried. 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959) was purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification.

Preparation and characterization of cationic hydrogels.

Cationic DMAAm semi-interpenetrated network structure hydrogels (semi-IPNs) were prepared by free-radical polymerization of DMAAm (2.0 mol/L) with MBAAm (10 mmol/L) in the presence of PDDA by using Irgacure 2959 (20 mmol/L) as photo-polymerization initiator. All chemicals dissolved into pure water and then the solution was degassed with sonication and aspiration. The concentration of charged group was fixed at 50 mmol/L. The degassed solution was poured into glass and silicon elastomer spacer mold. The intensity and irradiation time of UV light was 60 mW/cm^2 at 365 nm and 1 h, respectively. The mold was flipped each 15 min. During polymerization, the temperature of pre-gel solution was kept at 4 °C. PNIPAAm hydrogels were prepared by free-radical polymerization of NIPAAm as monomer and other conditions were the same with the preparation of DMAAm gel. The prepared hydrogels were washed with water for the removal of unreacted monomer and initiator. Young's modulus of each gels was measured by tensile test using tensile tester (Shimadzu EZ-Graph) in an ambient atmosphere. The tensile test was performed at 120 mm/min in tensile mode.

Formation of wrinkle structure on the hydrogel surface.

Wrinkle structures on the hydrogel surface were prepared by electrophoretic deposition of polymers. 50 μL of aqueous PSS solution (50 mmol/L) was put on the top of cationic hydrogel and then they were sandwiched with two Pt electrodes. An electric field was applied to these sandwiched solution and hydrogel. After electrophoresis, hydrogels were washed with pure water.

Characterization of the wrinkle surface.

We prepared fluoresce-labelled PSS (Flu-PSS) by copolymerization of SSNa and fluorescein-*o*-acrylate as fluorescence dye. Prepared Flu-PSS was purified by dialysis with regenerated cellulose dialysis membrane (Spectra/Por®, MWCO = 1kD) to remove unreacted monomers. The Flu-PSS was used as anionic polymer for wrinkle formation process. The fluorescence microscopic observation was performed using an IX-73 microscope (OLYMPUS) with a 20x LUCPLFLN 0.45 NA objective, and the expose time was 50 ms. The U-HGLGPS high pressure mercury lamp was used for excitation. As shown in **Fig. S1a** and **b**, the fluorescence from the wrinkling surface with electrophoresis of Flu-PSS was stronger than that of no-wrinkling surface without electrophoresis of Flu-PSS. This result suggests that PSS were deposited on cationic gel surface and formed polyion complex by electrophoresis.

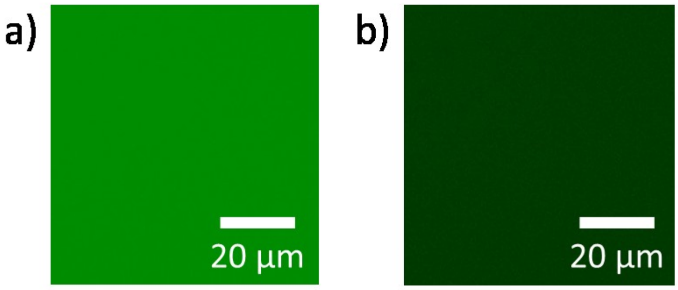

Fig. S1. Fluorescence microscopic observation of the hydrogel surface (a) with and (b) without electric field impression when Flu-PSS was used as anionic polymers.

Cross section images of wrinkle structures.

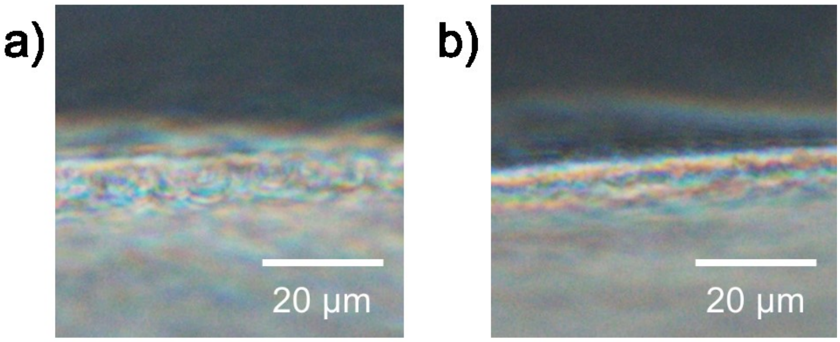

Fig. S2. Cross-section images of gradient wrinkling surface of Fig. 2e. (a) Left and (b) right side of gradient surface.

Rheological measurement of PNIPAAm gels.

A RheoStress 6000 from Thermo Fisher Scientific inc., operating in parallel plate geometry, was employed to measure the storage and loss moduli of the PNIPAAm gels. The top plate had a 20 mm diameter, while the bottom plate was a Peltier element, thermostatically controlling the system at 20 or 40 °C. The rheometer was operated in the stress-control mode with the frequency at 1 Hz for 300 sec. The measurements were performed in ambient atmosphere. Comparing of the storage modulus (*G*’) of PNIPAAm gels at 20 (**Fig. S3a**) and 40 °C (**Fig. S3b**), the *G*’ of PNIPAAm gels were increased from 290 to 4480 Pa by heating up to 40 °C. This modulus increasing of PNIPAAm gels were caused by aggregations of polymer chains above LCST.

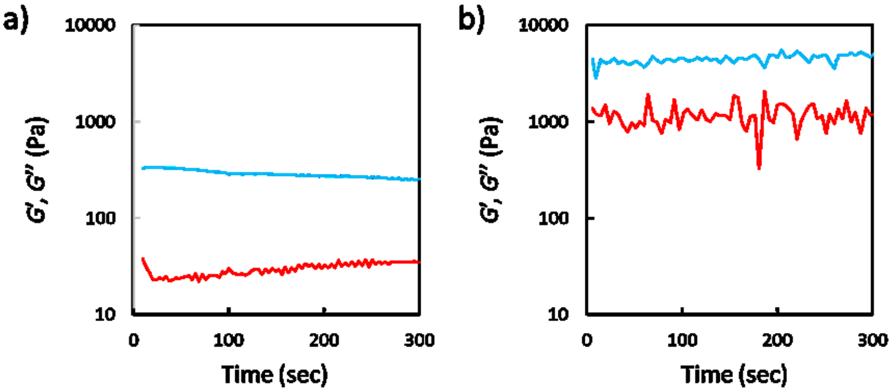

Fig. S3 (a, b) Temporal evaluation of storage modulus (*G*’, blue lines) and loss modulus (*G*’’, red lines) of PNIPAAm gel followed using rheology. The measuring temperature was (a) 20 °C and (b) 40 °C, respectively.