Wet-chemistry Based Hydrogel Sensing Platform for 2D Imaging of Pressure, Chemicals and Temperature

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Photos of the Master for Pyramidal Array and the Experimental Setup

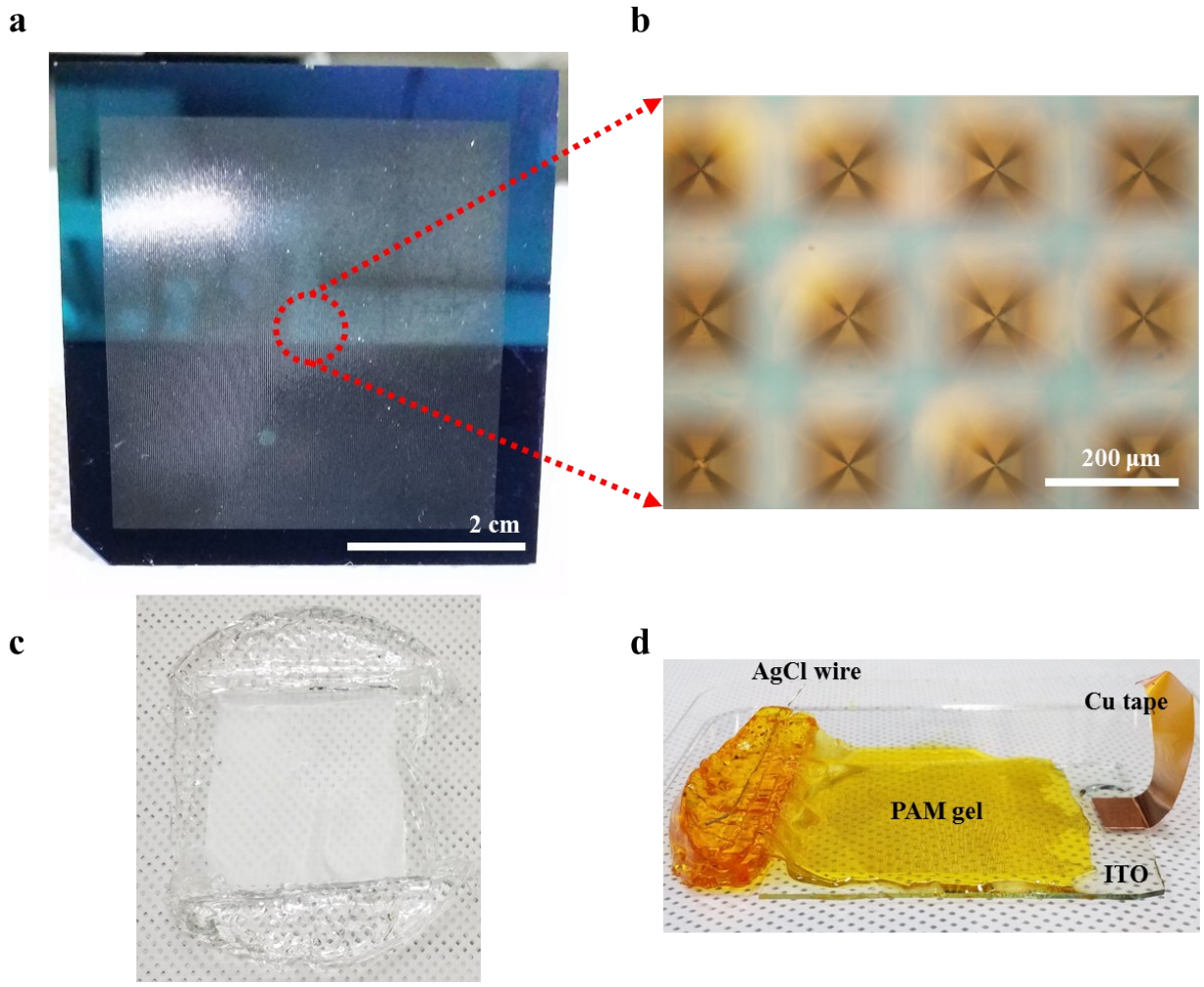

Figure S1. A silicone master for the hydrogel sensing platform. (a) A picture of pyramidal master fabricated by KOH anisotropic etching of silicon wafer coated with low stress nitride 2000 Å (size: 4.5 cm × 4.5 cm, single pixel diameter: 150 µm, 103 dpi). Scale bar, 2 cm. (b) A microscope image of pyramidal shape array. Scale bar, 200 µm. (c) Pyramidal array PAM gel before swelling. (d) Device setup for 2D imaging after 8 h swelling (2 electrode system, reference and counter electrode: AgCl wire).

Master fabrication.

The 200 nm of low stress silicon nitride (LSN) was deposited on polishing plane of silicon wafer (6 in) by chemical vapor deposition. The circle array (diameter: 150 μm) were fabricated on wafer by conventional photolithography process. The exposed part of the LSN by circle array mask was removed by dry etching in CF_3 and Ar. The remained photoresist was removed by O_2 plasma at 250 ℃. The KOH (1:1 [v/v] 45 wt% KOH solution/distilled water) anisotropic etching was performed using a LSN as mask to fabricate pyramidal shape array on the wafer at 83 ℃ for 2 h. This anisotropic etching generated the array of pyramidal trench on the silicon wafer, which is 150 μm in base length and 106 μm in height with 225 μm space between pyramids. The pyramidal silicon master was vapor-coated with trichloro(1H, 1H, 2H, 2H-perfluorooctyl)silane for 30 min to prevent adhesion between hydrogel and master. After fluorosilanization, the pyramidal hydrogel by UV cured was easily peeled from the master.

Composition of Electrolyte for Specific Stimulus.

$Ru(bpy)_3^{2+}$ /TPrA system	**$Ru(bpy)_3^{2+}$ / $C_2O_4^{2-}$ system**
$Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{3+} + e^-$	$Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{3+} + e^-$
$TPrA \rightarrow TPrA^{\bullet +} + e^-$	$C_2O_4^{2-} \rightarrow C_2O_4^{\bullet -} + e^-$
$TPrA^{\bullet +} \rightarrow TPrA^{\bullet} + H^+$	$C_2O_4^{\bullet -} \rightarrow CO_2^{\bullet -} + CO_2$
$Ru(bpy)_3^{3+} + TPrA^{\bullet} \rightarrow [Ru(bpy)_3^{2+}]^* + Pr_2\overset{+}{N}{=}CHEt$	$Ru(bpy)_3^{3+} + CO_2^{\bullet -} \rightarrow [Ru(bpy)_3^{2+}]^* + CO_2$
$[Ru(bpy)_3^{2+}]^* \rightarrow Ru(bpy)_3^{2+} + h\nu$	$[Ru(bpy)_3^{2+}]^* \rightarrow Ru(bpy)_3^{2+} + h\nu$

TPrA = $(CH_3CH_2CH_2)_3N$, bpy = $C_{10}H_8N_2$, Pr = $CH_3CH_2CH_2$, Et = CH_3CH_2

Figure S2. Chemical reaction equations in hydrogel sensing platform.

The Quantification of Pressure, Chemicals, and Temperatures

(1) Response Current to Pressure

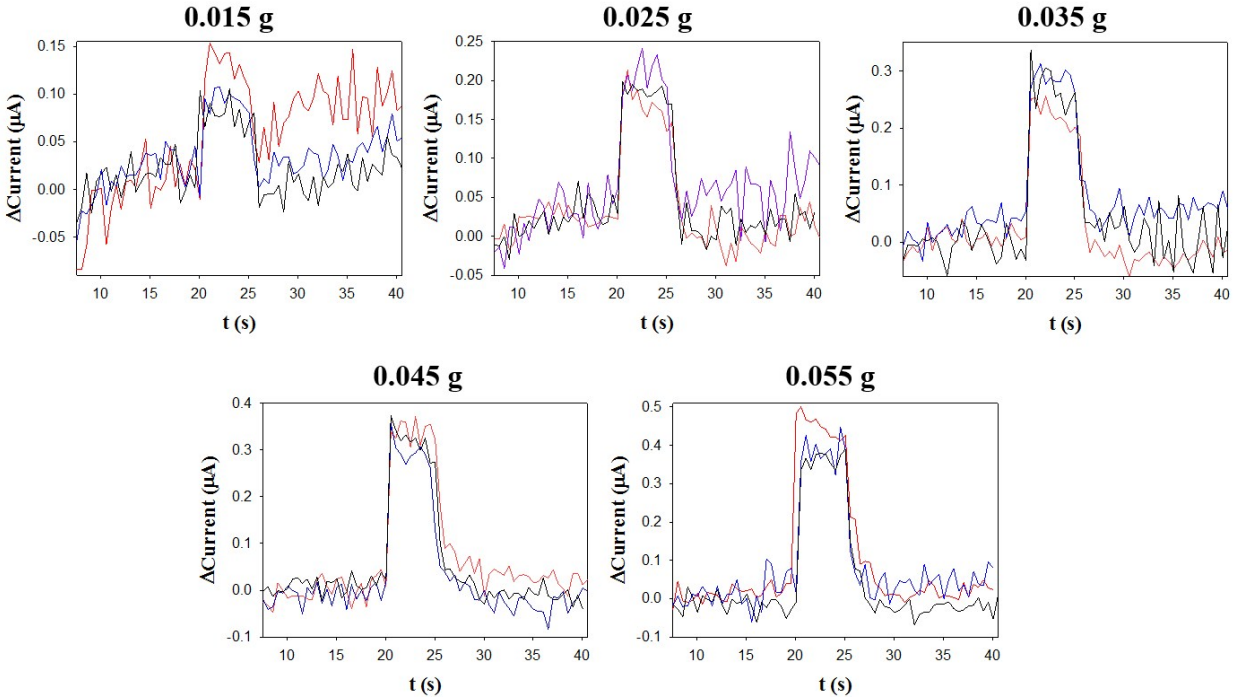

Figure S3. Response current to chopped papers with weight range 15-55 mg (10 mg intervals).

(2) Signal to Noise Ratio (Pressure)

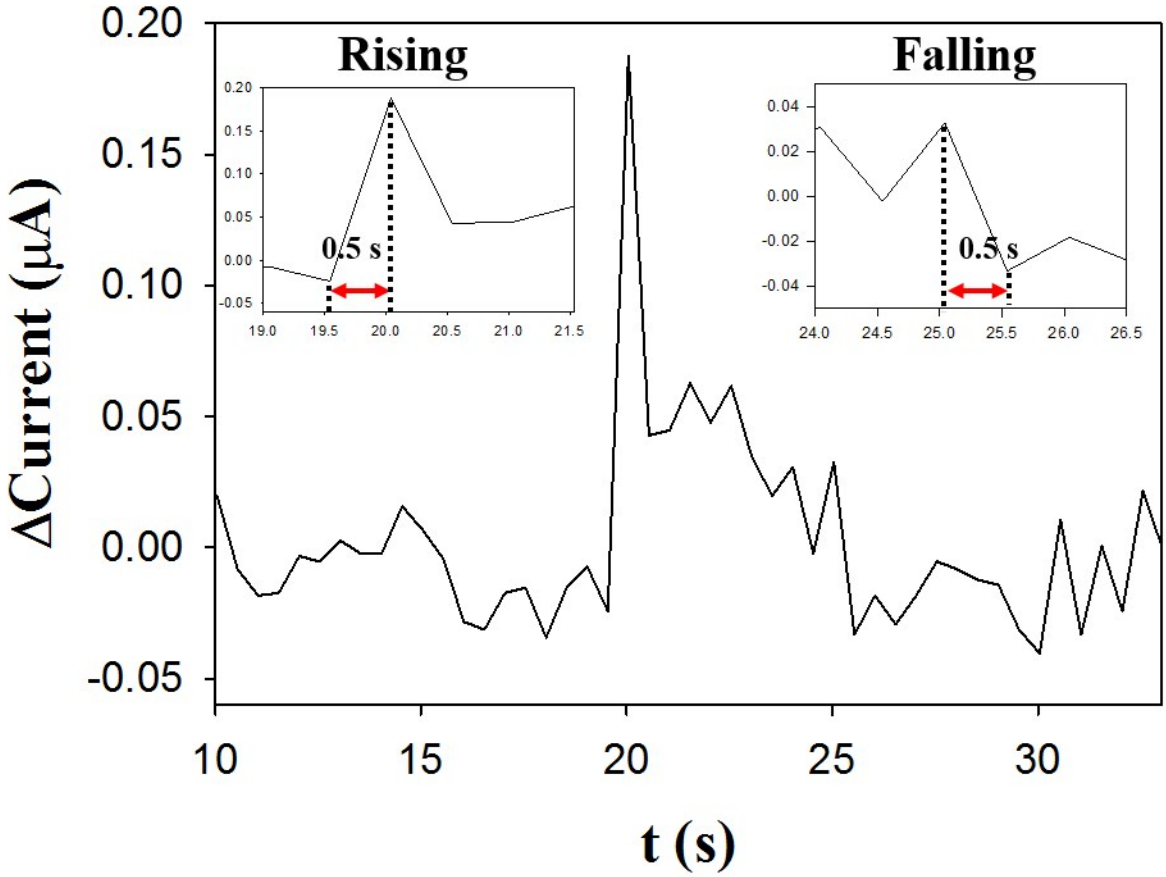

Figure S4. Response current to 0.01 g paper. Inset shows rising and falling current and response time seems to be ca. 0.5 s.

S/N ratio: 3 based on

Average value of signal (ca. 21.5 s ~ 23.5 s): 0.0453.

Standard deviation of background (ca. 10 s ~ 19 s): 0.0145 (3S: 0.0436).

(3) Intensity of ECL from raw images (Chemicals and Temperatures)

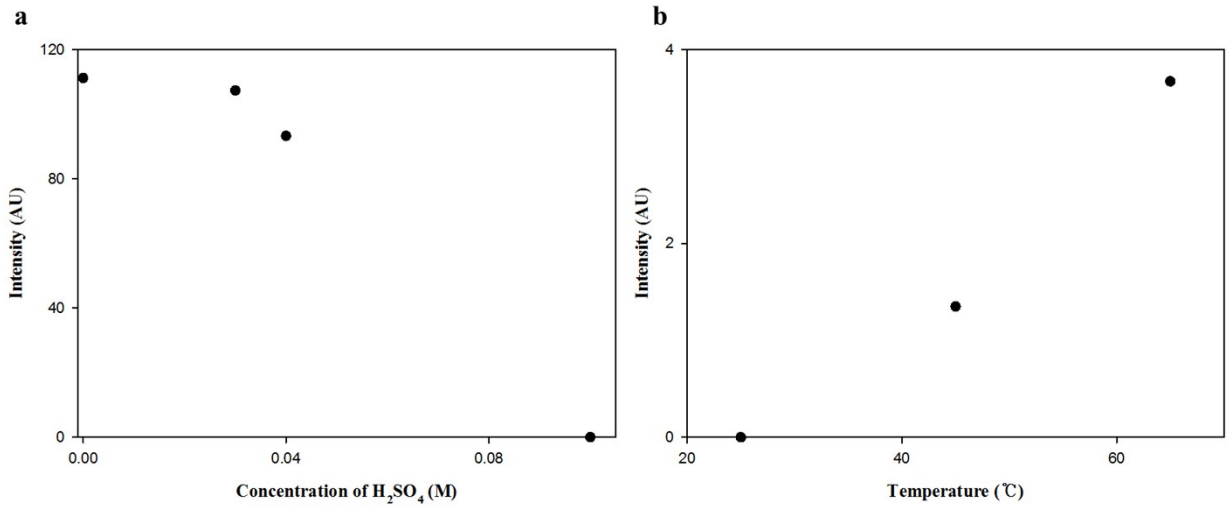

Figure S5. Intensity of ECL signal *vs.* external stimuli calculated from raw images (software: Image J, Function: Analyze-Measure-mean gray value). (a) Intensity of the sensor responded to H_2SO_4 (in Fig. 4a, after 5 min). (b) Intensity of the sensor responded to temperatures (in Fig. 4d).

Cycling Repeatability of Amperometric Sensor

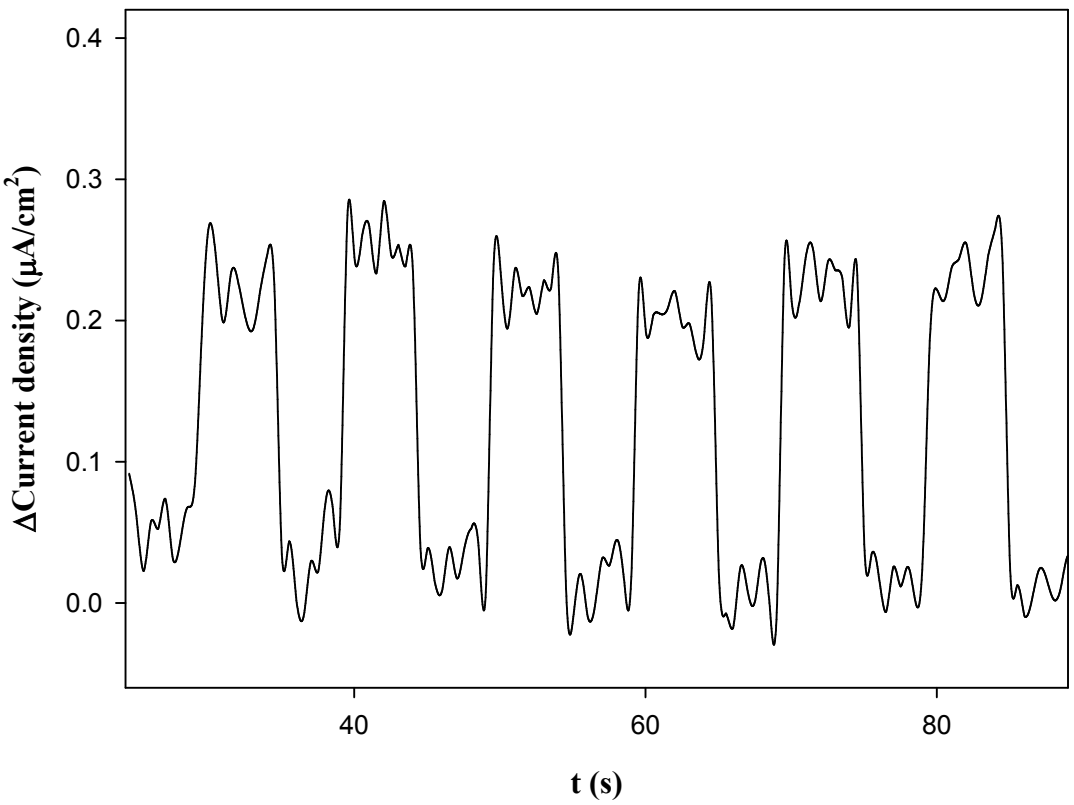

Figure S6. Response current upon the repeated loading/unloading of 0.065 g paper.

The separately uploaded Movie File

The movie of optical microscope on pyramidal hydrogel shows the reversible deformation/restoration of the pyramid upon the repeated loading/unloading of each weights (1, 2, 10 g).

The Fabrication of Pressure Sensor Integrated into Conventional Electronics

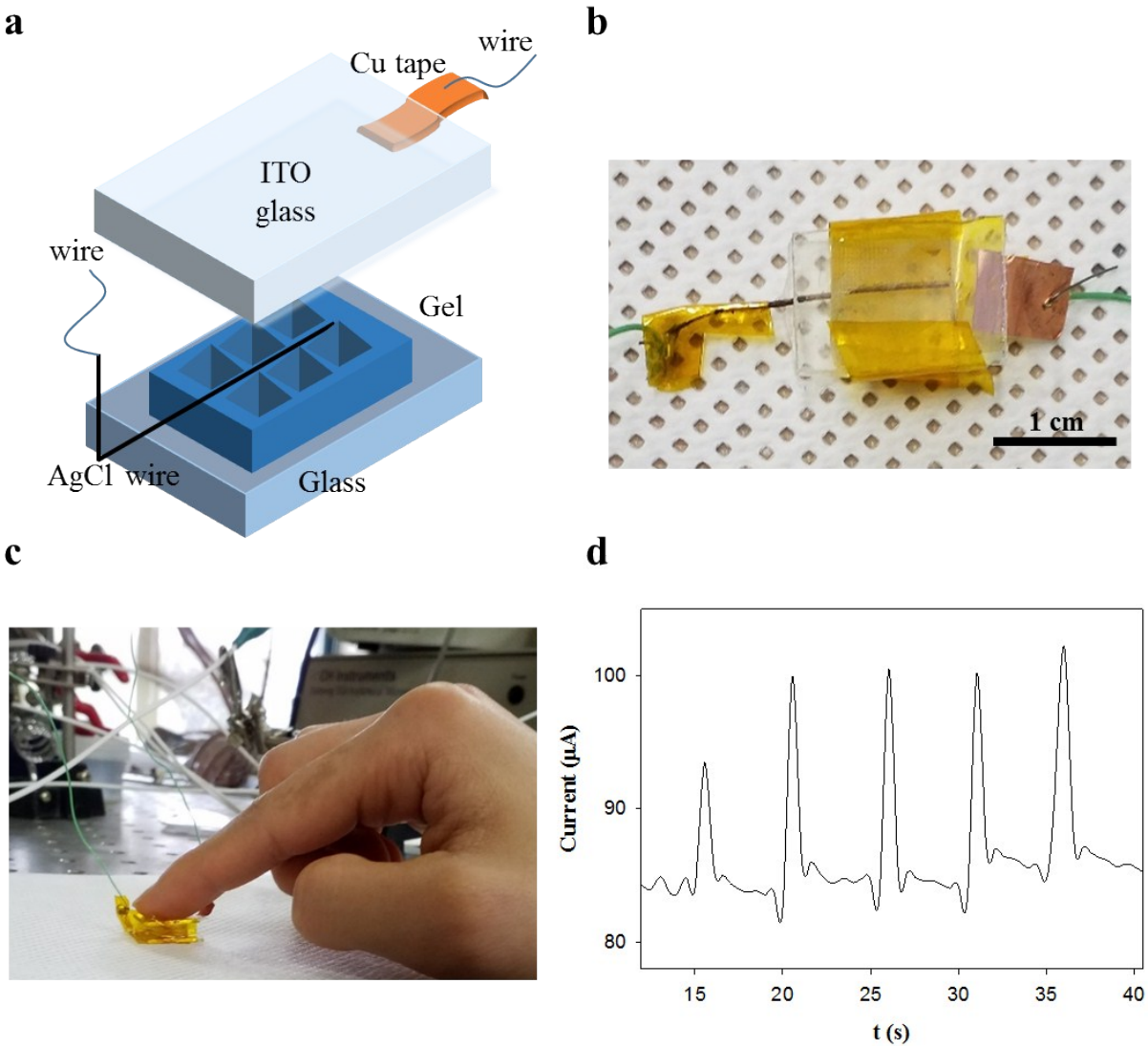

Figure S7. (a) The schematic illustration of conventional two-terminal sensor for pressure (2 electrode system, electrolyte inside gel: 0.9 mM FcMeOH in 3 M NaCl) (b) The photo of experimental set-up. Scale bar, 1 cm. (c) The photo of the sensor under operation by fingertip. (d) Response current of the sensor by fingertip touch.

Durability of Amperometric Sensor against Evaporation of Water

The content of water within the hydrogel decrease by the evaporation. The evaporation process was monitored from the mass change. We prepared the cube of PAM (3.5 cm × 3.5 cm × 0.5 cm) with the same composition of electrolyte for Fig. 1. After the removal of excess electrolyte on the surface by blowing N_2 flow, the mass change of the cube placed on the petri dish were measured. In the presence of the cover of the dish (not tightly sealed), ca. 4.8 % of water is lost after 5 hours while ca. 14.5 % of water evaporated without the cover.

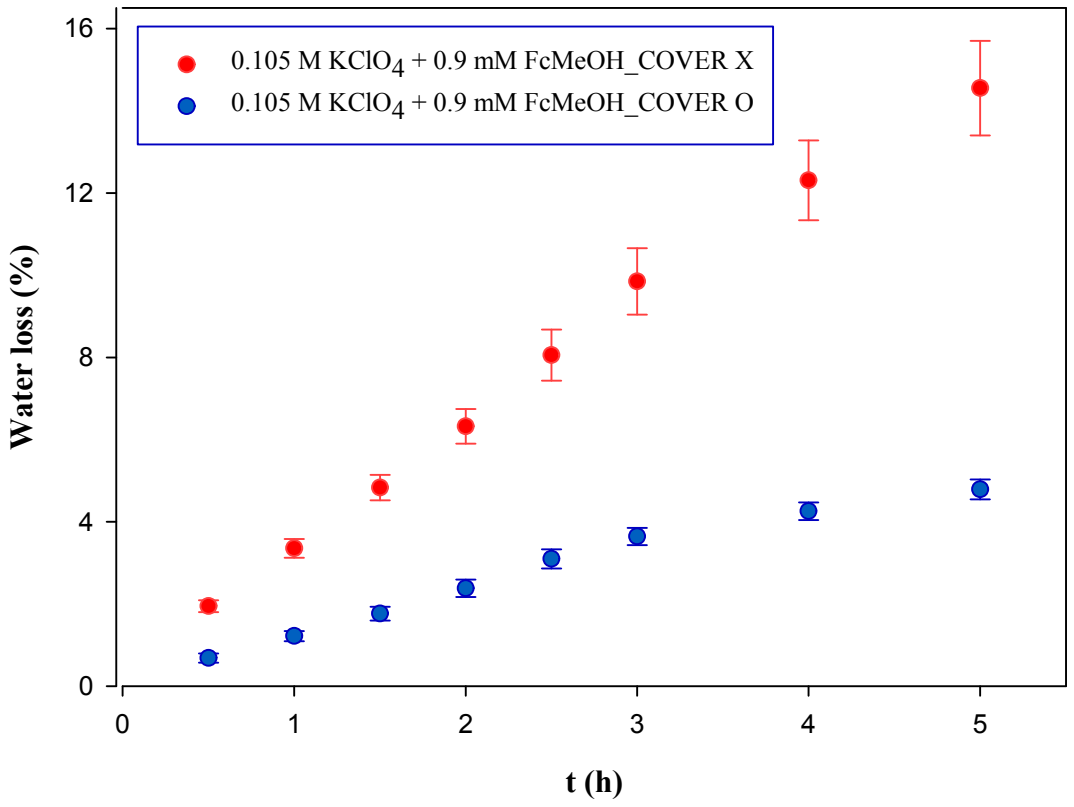

Figure S8. Evolution of water loss with time for hydrogel cube (3.5 cm × 3.5 cm × 0.5 cm) filled with 0.105 $KClO_4$ and 0.9 mM FcMeOH with the cover of petri dish (blue) without the cover (red).

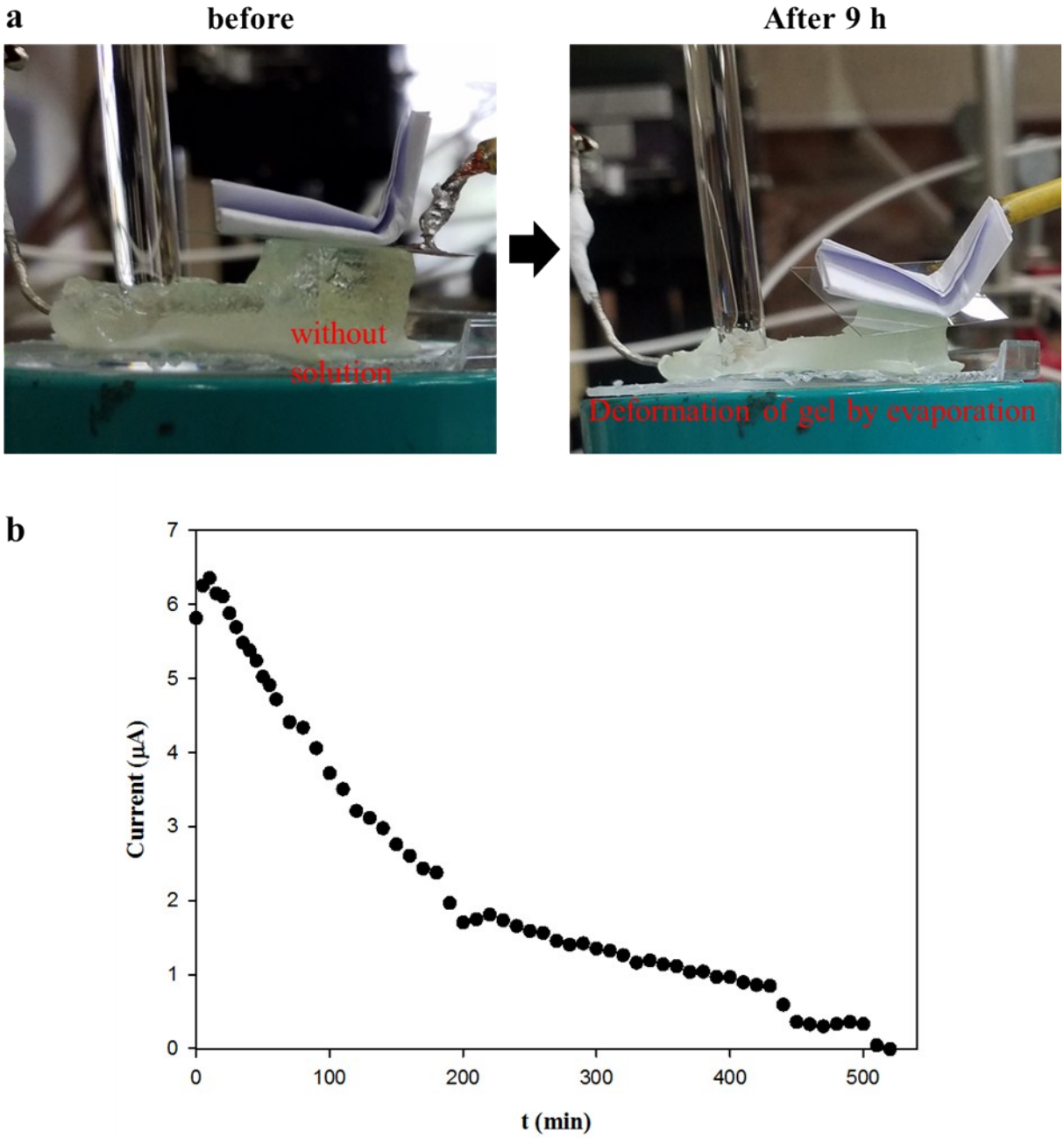

Figure S9. (a) The photo of amperometric sensor for pressure without the surrounding electrolyte solution to measure durability against evaporation of water. (b) The current signal with time.

Raw Images before image processing

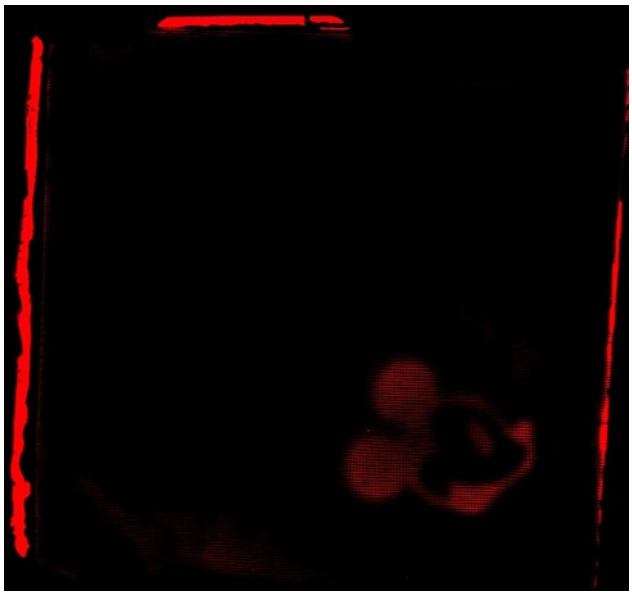

Figure S10. A original 2D image adjusted brightness and contrast by ImageJ.

The Images of Pressure without Pyramidal Structure (Flat Gel)

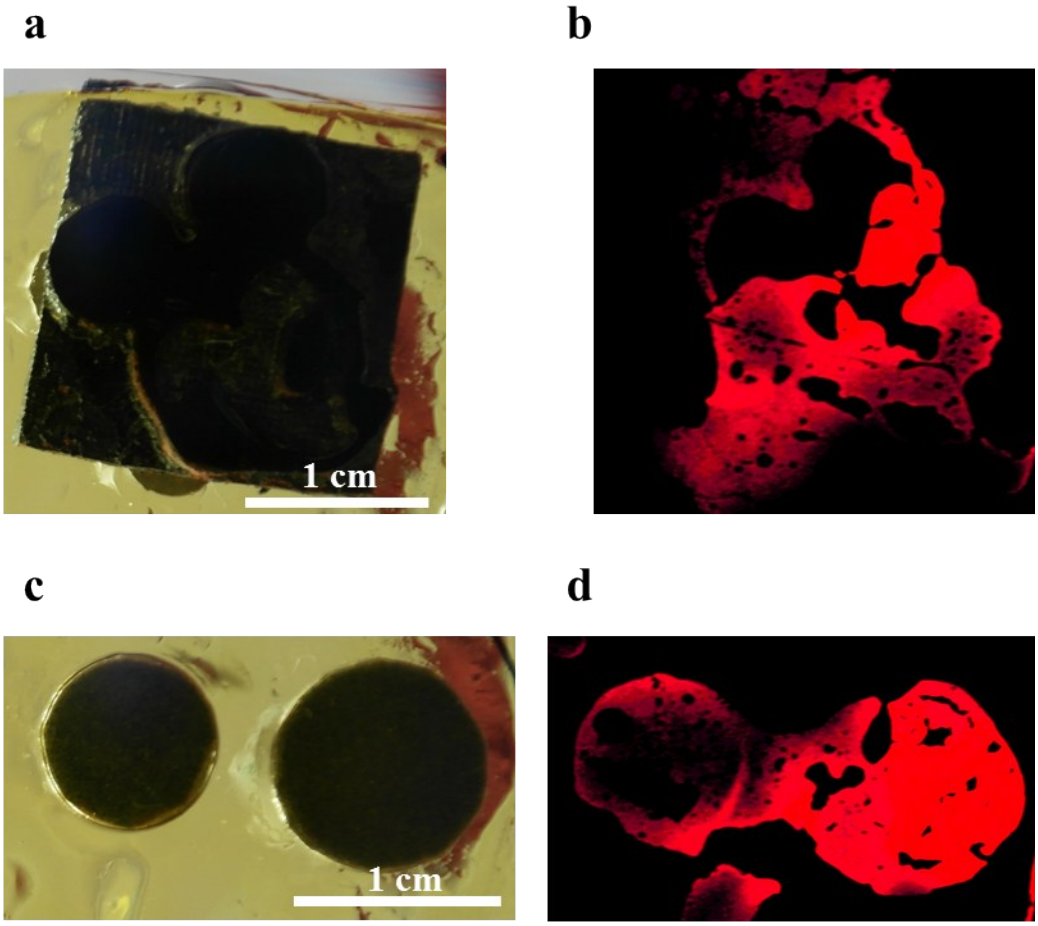

Figure S11. A 2D imaging from the electrochemical cell composed of unstructured hydrogel (flat hydrogel without pyramid array). A photo of ECL cell (a) and ECL image of the "Mickey Mouse" stamp (1.87 g) and weight (8 g) (b). A photo of ECL cell (c) and ECL image of two weight (5 g and 10 g) (d).

Additional Images for Pressure Sensing

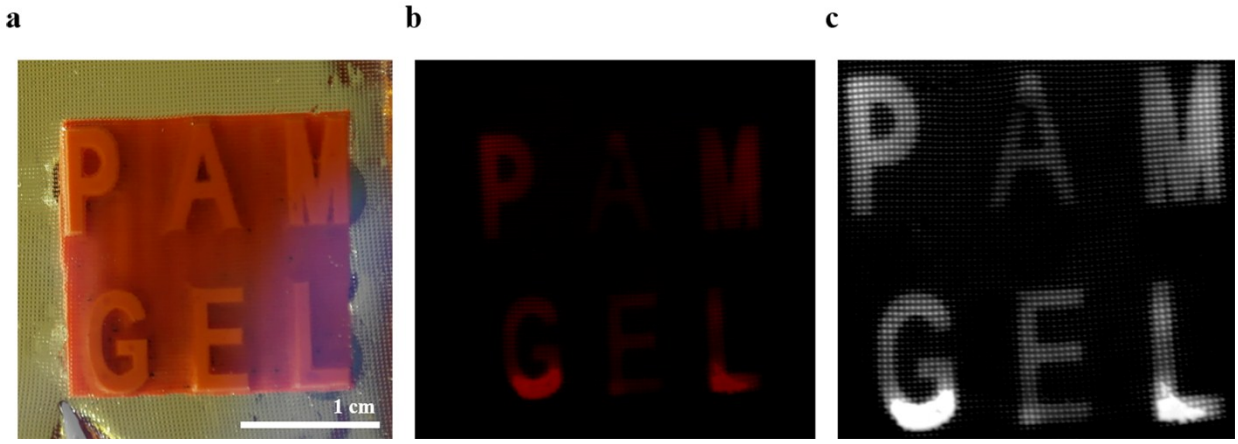

Figure S12. A 2D imaging of alphabet pattern "PAM GEL". (a) A picture of the "PAM GEL" stamp (1.98 g) and weight (6 g). Scale bar, 1cm. (b) Original ECL image without processing. (c) A red channel image adjusted with brightness and contrast.