Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Hydrogel Pen for Electrochemical Reaction and Its Applications for 3D Printing

Hosuk Kang,[a§] Seongpil Hwang, [*b§] and Juhyoun Kwak[*a]

[a] Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST),
Daejeon 305-701, Republic of Korea

[b] Department of Advanced Material Chemistry, Korea University, Sejong 339-700, Republic of
Korea

Contents

Fabrication of Silicon master of agarose tip

Pyramidal holes with square base (200μm x 200μm) were fabricated on Si wafer through the lithography process, based on the protocol reported by Mirkin group [S1]. 200nm of low stress silicon nitride (LSN) film was formed on cleaned Si <100> wafer by chemical vapor deposition. The circle (r=100μm) patterns were prepared by photolithography using photoresist and developing solution. The exposed part of LSN film through the circle pattern is removed by dry etching in CF_4 and Ar gas. Photoresist were stripped in O_2 plasma at 250 ℃. The organic residues were cleaned in piranha solution (3:1 [v/v] H_2SO_4/H_2O_2). The pyramidal holes on Si wafer were prepared through the process of silicon anisotropic etching using LSN film as a mask in 20% KOH solution at 83 ℃ for 7hours. The etching solution was vigorously fluxed by pumping in the reaction chamber. The residual LSN around circle patterns were mechanically removed by repetitive agarose tip preparation. Pyramidal holes were examined by scanning electron microscopy (SEM) and the apexes of pyramids were confined in 200 nm region.

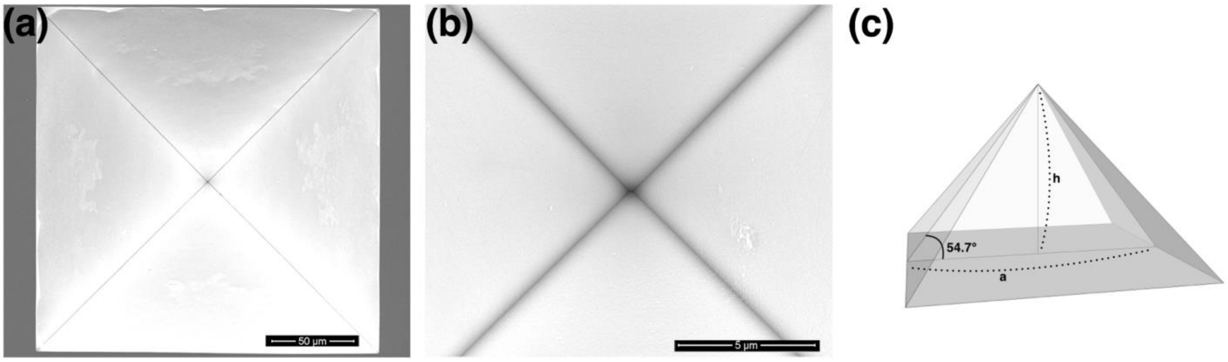

Figure S1. (a, b) SEM image of Si microhole. (c) optical microscopic image of agarose tip.

Determination of the mass transport behavior within agarose

Microdisk electrode preparation

Microdisk electrode was polished with water-suspended 15µm, 6µm, 3µm, 1µm polishing diamond and 0.05µm polishing alumina sequentially on micro-cloth pad and polished with 1µm and 0.05µm alumina repeatedly prior to every measurement. The repeated polishing of microelectrode shows reproducible results in cyclic voltammetry of 1mM ferrocenemethanol and 0.1M KCl solution.

Determination of mass transport coefficient within agarose

The mass transport coefficient in agarose was determined by the measurement of redox reaction on Au microdisk electrode(r=5µm) contacted on agarose surface. Steady-state current was measured from cyclic voltammetry and chronoamperometry. From the measured steady-state current, the mass transfer coefficient (m) can be obtained from following equations (1,2).

$$i_{ss} = 4nFDCr \quad (1)$$

$$m = DC \quad (2)$$

(n : electron number, F : Faraday constant, D : diffusion coefficient, C : concentration of redox species, r : radius of the disk electrode, m : mass transport coefficient)

The steady-state current was measured from the microdisk electrode in contact on agarose surface. The agarose samples used for measurement had been soaked in the ferrocenemethanol solution containing electrolyte for 2-8 hours and the equilibrium is established at 8hours (Figure S2). The ratio of mass transport coefficient in the gel and in the solution, m_{gel}/m_{sol} was determined as 0.934 ± 0.014. (Figure S3)

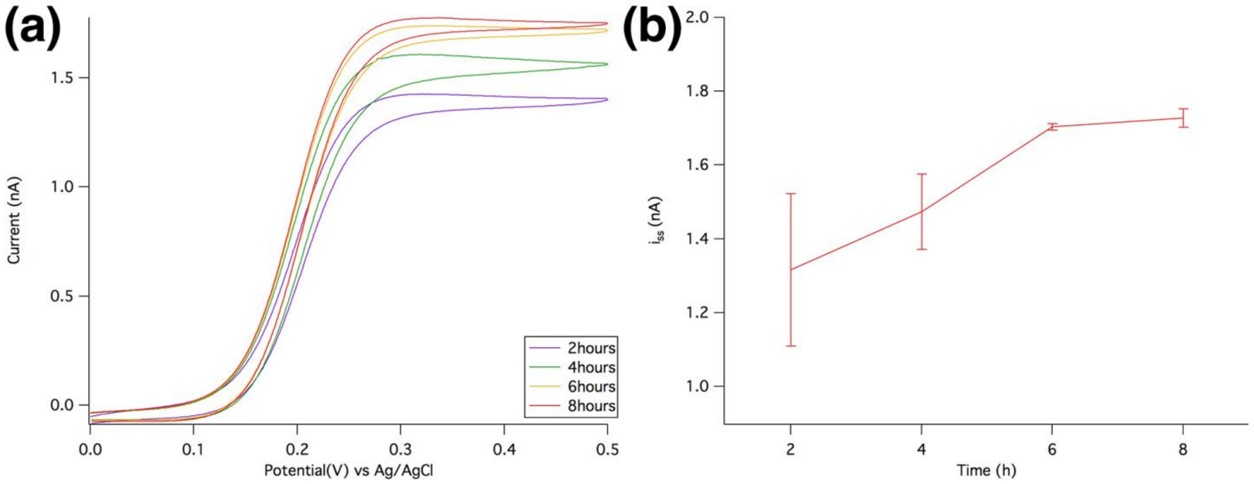

Figure S2. (a) Typical cyclic volatmmograms from Au microdisk electrode (r=5µm) contacted on agarose containing redox molecules and electrolyte. (2 – 8hours of soaking time in 30 times volume of 1.65mM ferrocenemethanol and 115mM KClO4 aqueous solution) (b) Steady-state current vs soaking time plot.

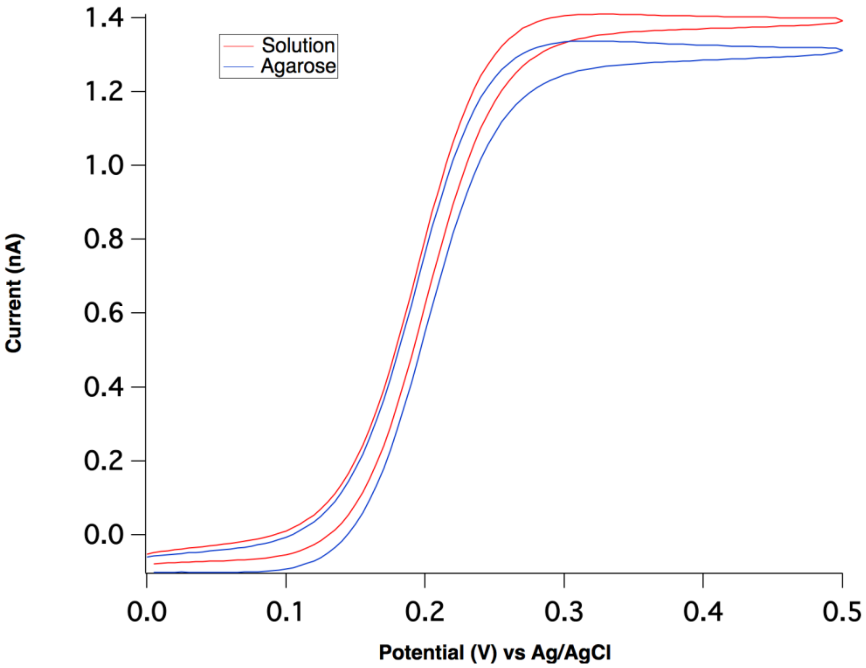

Figure S3. Typical cyclic voltammograms obtained from the microdisk electrode (r=5µm) in soaking solution (red) and on agarose surface (blue). Soaking solution : 1mM ferrocenemethanol and 115mM KClO4. The agarose have been soaked in the soaking solution for 8hours before the measurement.

Simulation method about mass transport behavior within HYPER

COMSOL Multiphysics 4.4 with Chemical Reaction Engineering Module was employed to simulate the mass transfer based on Fick's law of diffusion. A geometry for a simulation of HYPER as depicted in Fig. 2. (A) can be easily built by selecting 'Pyramid' from the 'More Primitives' under the 'Geometry toolbar'. COMSOL solves the diffusion equations in Cartesian coordinate system, $\nabla \cdot \left(-D_i \nabla c_i\right) = 0$ for stationary problem or $\frac{\partial c_i}{\partial t} + \nabla \cdot \left(-D_i \nabla c_i\right) = 0$ for time dependent problem. For a redox couple, Ox and Red species, 2 species are considered, index 1 for ferrocenemethanol and 2 for oxidised form of ferrocenemethanol. The Dirichlet boundary concentration conditions at the semi-infinite surface (upper square in Fig. 2. (A) are $c_1 = C_R^*$ and $c_2 = C_O^* = 0$. The Dirichlet boundary concentration conditions at the ultramicroelectrode surface (lower square in Fig. 2. (A)) follow nernstian, i.e. $c_1 = c_2 \theta^{-1}$ where $\theta = \exp\left[(F/RT)(E_{appl} - E^{0'})\right]$ and $c_2 = C_R^* - c_1$ assuming $D_O = D_R$. For the chronoamperometry for diffusion-limited diffusion, $E_{appl} - E^{0'} >> 0$. For the linear sweep voltammetry, $E_{appl} = E_i + \upsilon t$. After or during the simulation, the current at the ultramicroelectrode can be obtained by integrating the normal diffusive flux of species 1 (ndflux_c$_1$) throughout the lower square in Fig. 2. (A) and multiplying Faraday constant. The dependency on *d*, which is the compressed length of HYPER, can be easily obtained by parametric sweep of *d* in the geometry of HYPER.

Plastic deformation of agarose tip in limited strain

The plastic deformation of HYPER in our experimental condition is examined by repeated approach – retraction of agarose tip to electrode surface. The approach depth was controlled 1~3μm by 1μm. Figure S5 shows the three repeated approach curves. 3μm in height of the tip was deformed by approach and recovered after retraction in each approach - retraction. The geometry of the end of tip determines the approach curve profile and current increment value at each approach depth change. Although, there are some difference between the current scale of approach step and retraction step, entire repeated approach – retraction curves show very similar shape and current scale. This result suggests that the agarose tip recover to its nearly initial geometry after 3μm compression and subsequent release. In addition, it is reported that high viscous agarose have the failure strain value, 0.43[S2].

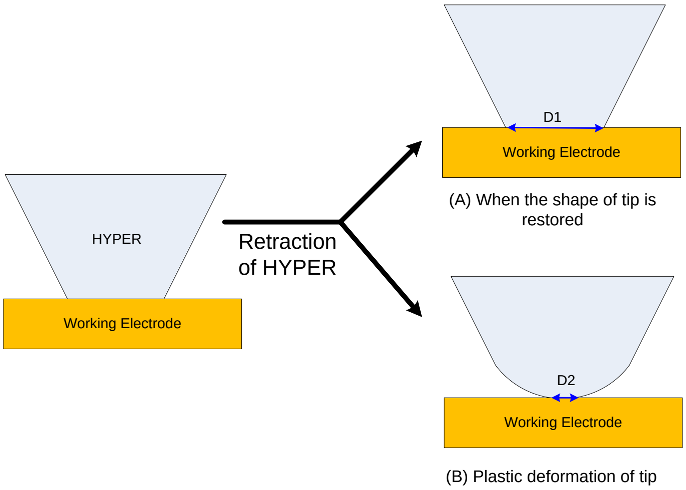

Figure S4. Schematic diagram of HYPER during the retraction of tip (A) when the shape of tip is restored and (B) when the plastic deformation of tip makes tip dull. Smaller diameter of contact area of dull tip induces larger decrease in faradic current during the retraction than that during approaching.

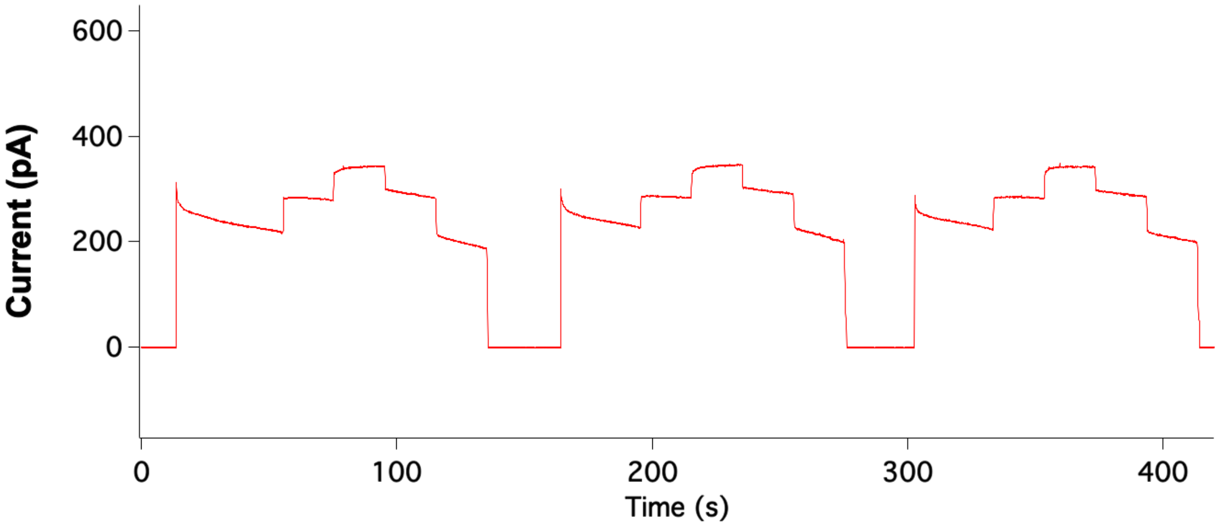

Figure S5. Typical three sequential repeated approach - retraction curves from HYPER tip. 3 times of approach (3µm) and retraction (3µm).

Dehydration effect of agarose tip

The dehydration effect of HYPER over relatively long time exposure to air (0~40min) is tested. The most part (over 90% height) of agarose body mounted to electrochemical cell is immersed in the soaking solution to minimize the dehydration of agarose. The relative humidity was maintained as 55%. Prior to electrochemical measurements, pyramidal agarose tip mounted to cell were exposed to air for 0~40min. Figure S6 is obtained cyclic voltammograms at various dehydration time and same contact area between agarose tip and electrode surface. We can conclude that the effect of dehydration on electrochemical result is negligible in conducted time scale (40min). Additionally, the most approaches and measurements were finished in 10min after mount of agarose tip and the effect of dehydration on our results is very small.

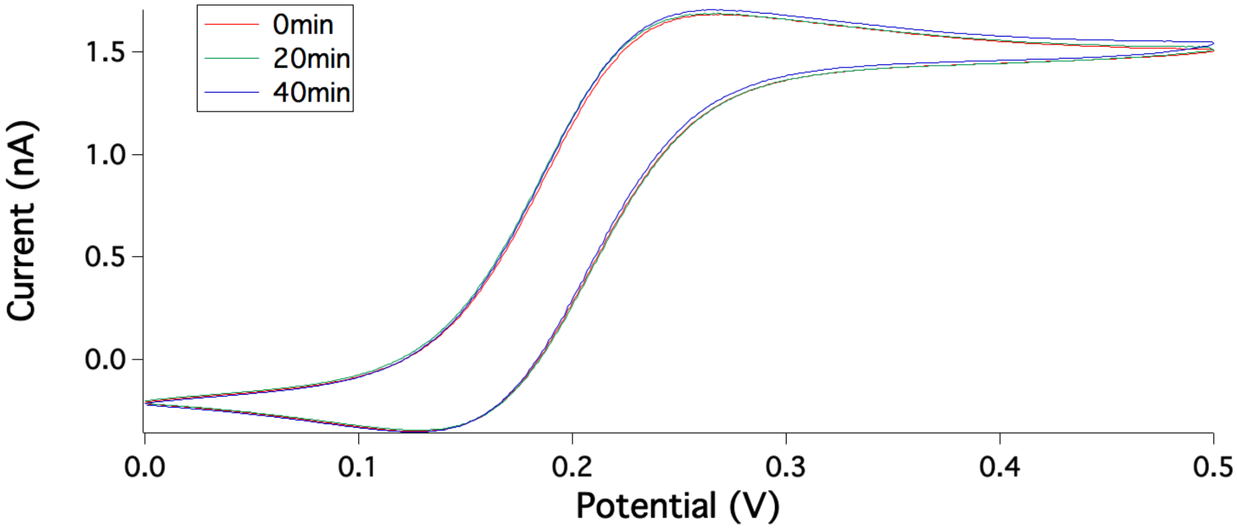

Figure S6. Cyclic voltammograms dependent on exposed time of HYPER tip. Approach depth : 10 μm

Scanning electrochemical microscope (SECM) using HYPER as probe

Kodak gold compact disc was used for surface scanning by constant height mode in commercial SECM. Prior to scanning, the protective layer of CD surface was removed in nitric acid (60%, 1min), washed by distilled water and dried by nitrogen gas. Exposed gold layer of CD was used as working electrode. The response current is determined by the contact area between HYPER tip and CD surface from eq. 1 in manuscript which is affected by topology of CD surface and an offset angle between surface and the probe. The high resolution (40nm) image of CD surface was obtained using HYPER as probe with commercial SECM instruments without any modification.

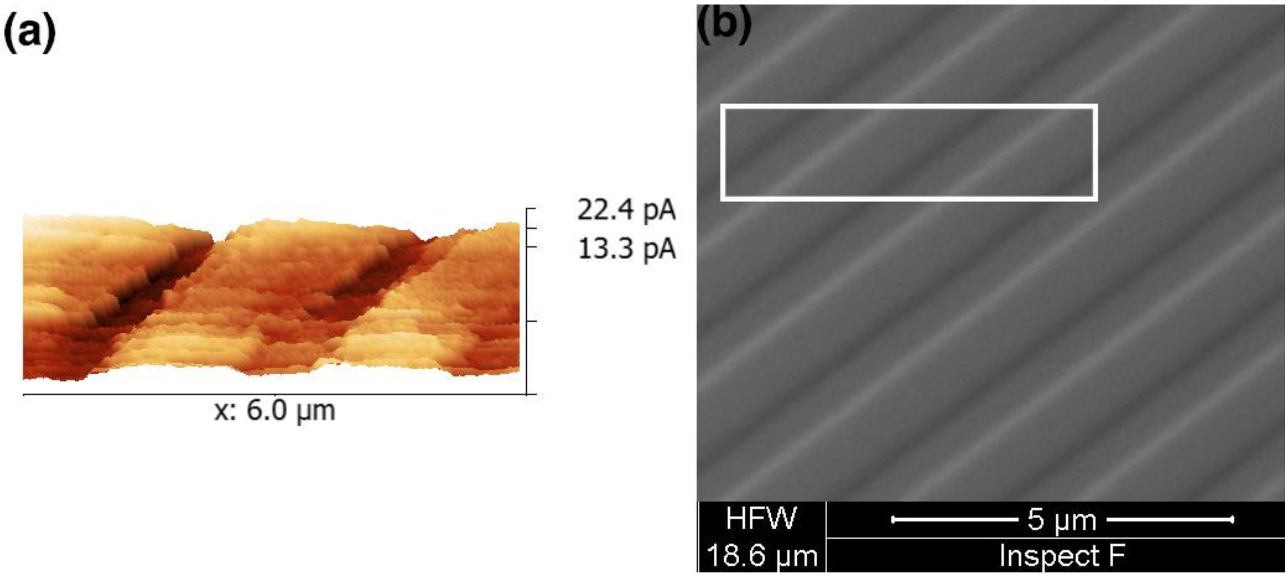

Figure S7. (a) Scanning electrochemical microscopic image. (b) SEM image of CD surface topology.

Electrodeposition of platinum using HYPER

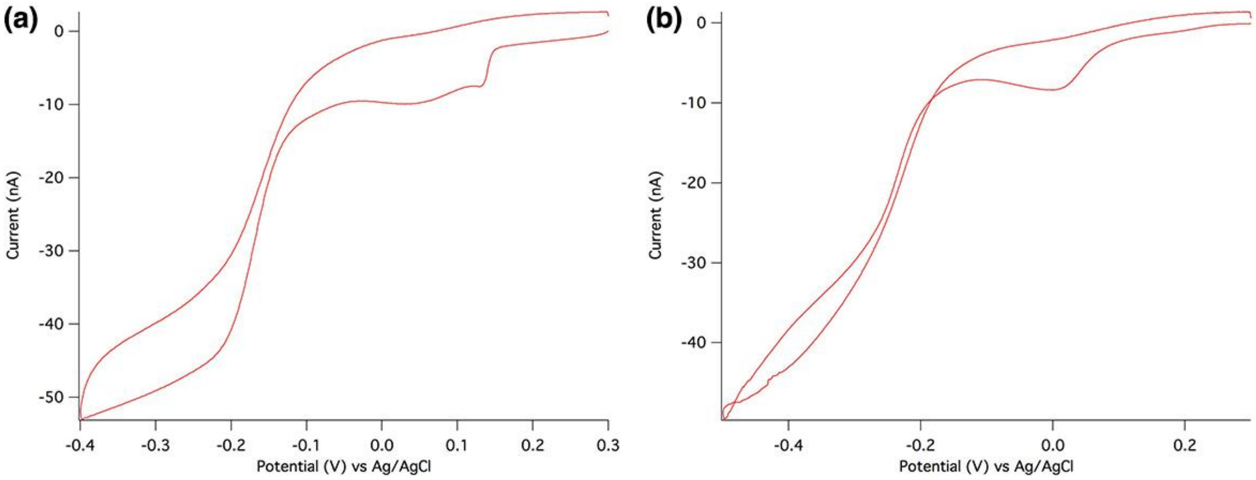

Figure S8. Cyclic voltammogram obtained (a) at Au microdisk electrode (r = 5µm) in 5 mM K_2PtCl_4 and 115 mM $KClO_4$ solution (b) Au coated Si wafer contacted with hydrogel containing Pt ions (Soaked in 20 mM K_2PtCl_4 and 115 mM $KClO_4$ solution for 2 h). Approach depth : 10µm

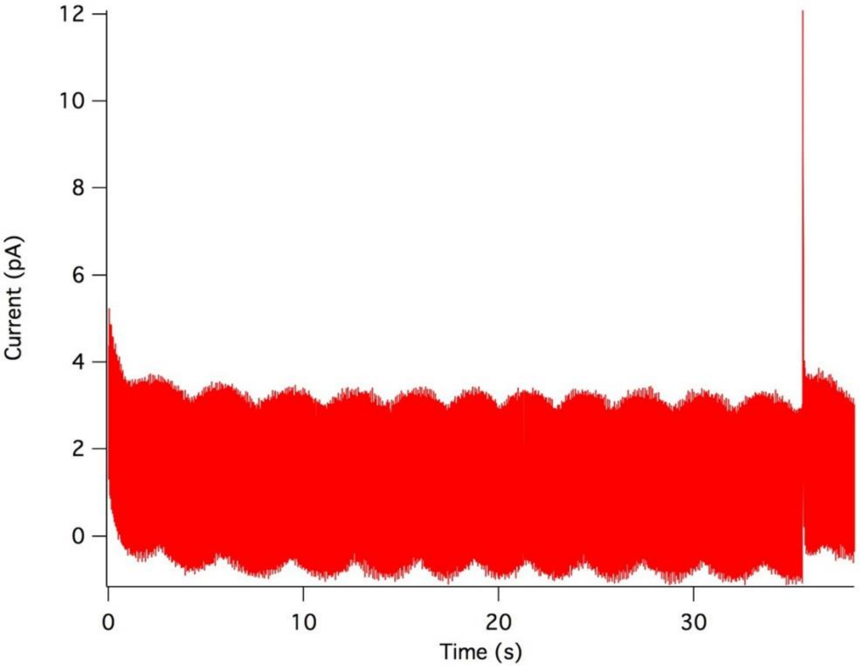

Figure S9. Charging current feedback when hydrogel tip contacts on working electrode surface

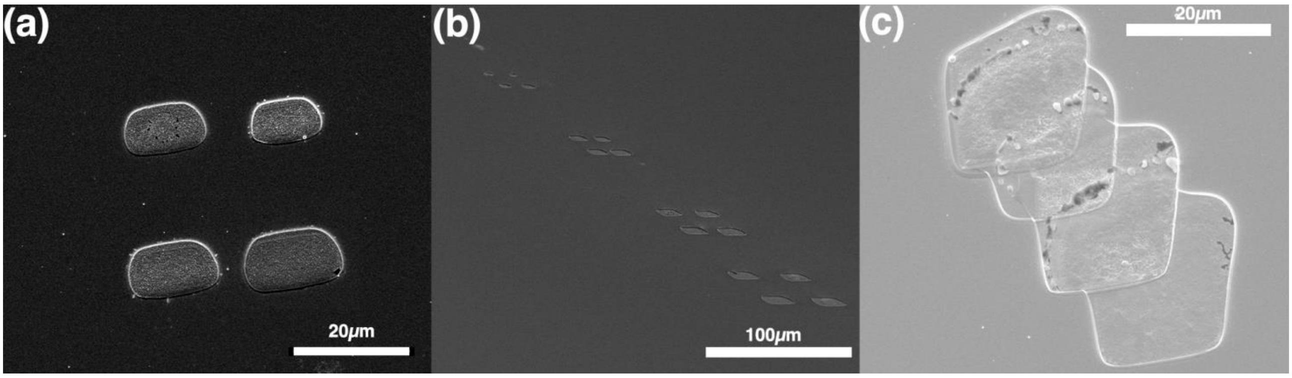

Figure S10. (a) SEM image of printed plate array (2x2) (b) printed arrays (2x) in various scale (c) Sequentially printed plates in linear direction.

References

S1. F. Huo, Z. Zheng, G. Zheng, L. R. Giam, H. Zhang, and C. A Mirkin, *Science*, 2008, **321**, 1658–1660

S2. D. L. Lootens, E. Amici, and K. P. Plucknett, 2000, 730–738