

Supporting Information

Programmable Electrochemical Rectifier Based on a Thin-Layer Cell

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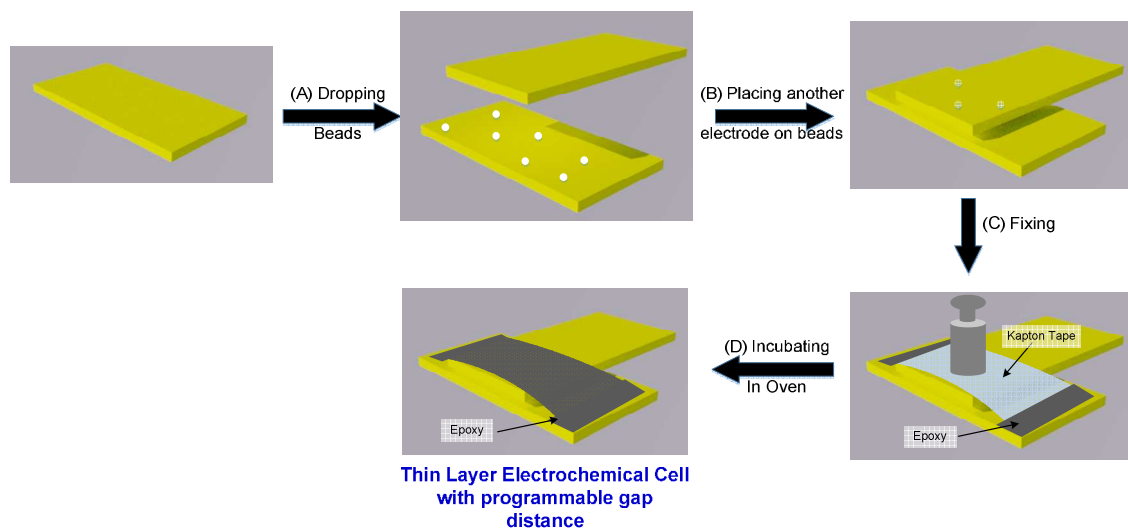
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Scheme S1. Schematic diagram of the fabrication process of thin layer electrochemical cell based on beads as a spacer.

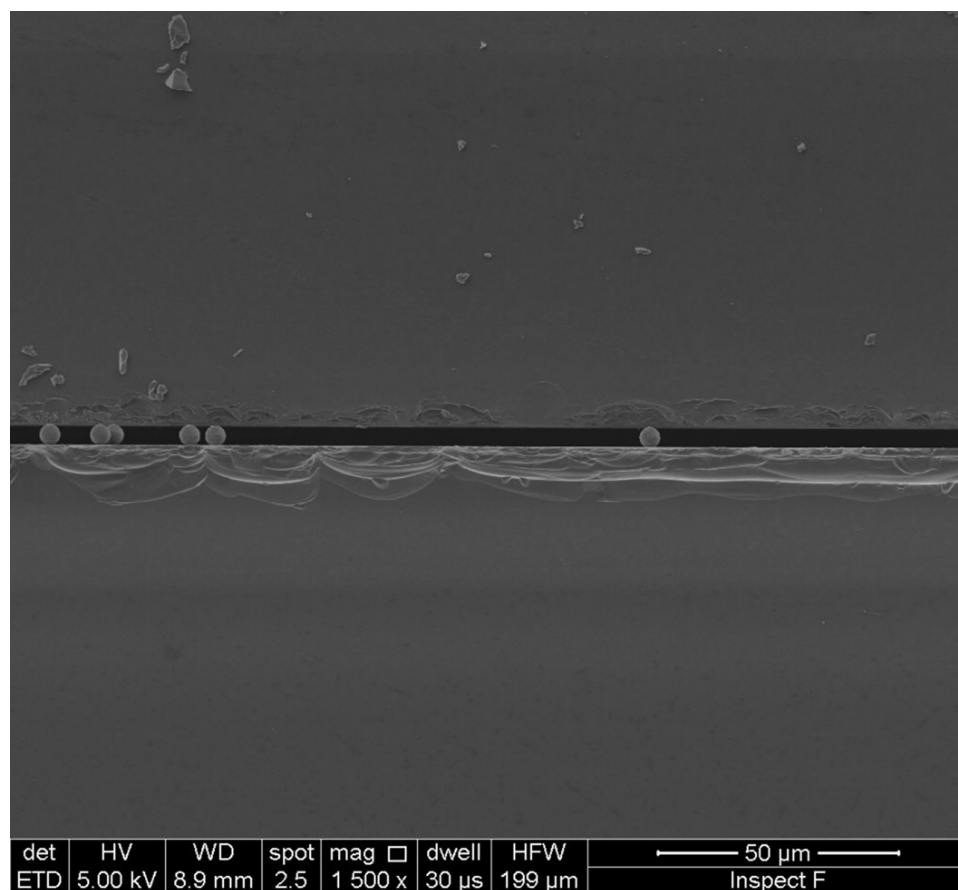
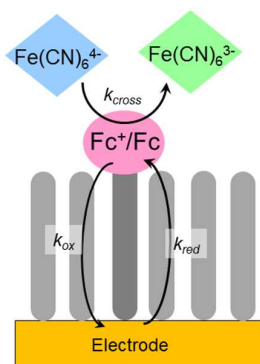


Figure S1. Representative SEM image of the 4 μm gap fabricated by our process.

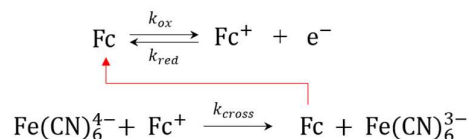
Interpretation on Steady-state current of ferrocene-modified SAM with ferrocyanide in thin layer electrochemical cell

The steady-state currents of rectifying devices are obvious as shown in Figure 2 of the manuscript. We proceed to estimate the steady-state currents with the relevant parameters responsible for electrochemical rectification, which is modeled by Alleman-Weber-Creager Approach (AWC approach). (see Ref. 11, 40 in the manuscript)



< **Scheme S2.** Illustration of electrochemical rectification mediated by ferrocene >

Step 1 : Scheme S2 is a simple physical model for electrochemical oxidation of $\text{Fe}(\text{CN})_6^{4-}$ by an immobilized Fc^+/Fc . The heterogeneous first-order rate constants for reduction and oxidation of the immobilized ferrocene are k_{red} and k_{ox} , respectively. The homogeneous second-order rate constant for reaction of $\text{Fe}(\text{CN})_6^{4-}$ with Fc^+ is k_{cross} . Note that $\text{Fe}(\text{CN})_6^{4-}$ is practically nonelectroactive due to the blocking behavior of SAM although $\text{Fe}(\text{CN})_6^{4-}$ is electroactive in typical electrochemical experiments. The following describe the electrochemical oxidation of a nonelectroactive species in electrolyte by a immobilized ferrocene which is called catalytic (EC'') reaction.

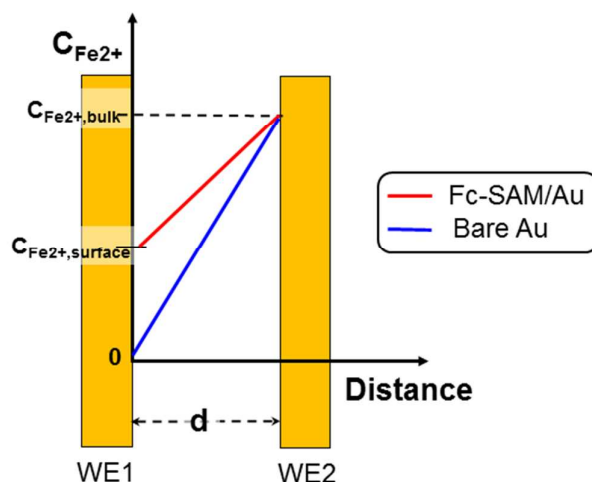


The overall reaction can be written by

$$\frac{i}{FA} = k_{cross} C_{\text{Fe}2+, \text{surface}} \Gamma_{\text{Fc}^+} \quad (\text{Eq. S1})$$

Where i is the current, F is the Faraday constant, $C_{\text{Fe}2+, \text{surface}}$ is the concentration of ferrocyanide at electrode surface, and Γ_{Fc^+} is the concentration of Fc^+ at electrode surface.

Step 2 : Figure 2 in the manuscript shows the steady-state current at sufficient positive potential, indicating that $C_{\text{Fe}2+, \text{surface}}$ is a time-independent constant with thin layer electrochemical cell under experimental condition as shown in Scheme S3.



< **Scheme S3.** Illustration of concentration gradient within thin layer electrochemical cell >

It can be written by

$$\frac{\partial C_{\text{Fe}2+, \text{surface}}}{\partial t} = D_{\text{Fe}2+} \frac{\partial^2 C_{\text{Fe}2+, \text{surface}}}{\partial x^2} = 0$$

where D_{Fe2+} is the diffusion coefficient of ferrocyanide and then

$$D_{Fe2+} \frac{\partial C_{Fe2+,surface}}{\partial x} = \frac{D_{Fe2+}}{d} (C_{Fe2+,bulk} - C_{Fe2+,surface}) \quad (\text{Eq. S2})$$

where $C_{Fe2+,bulk}$ is constant due to applied potential at working electrode 2. Then,

$$i = \frac{FAD_{Fe2+}}{d} (C_{Fe2+,bulk} - C_{Fe2+,surface}) \quad (\text{Eq. S3})$$

Thus, the steady-state current rely on the concentration gradient at working electrode 1, which depends on the surface concentration of ferrocyanide at electrode surface. When the enough potential for the oxidation at working electrode 1 at bare Au, the surface concentration approaches to 0. In contrast, $C_{Fe2+,surface}$ on Fc-SAM/Au will be governed by the coverage of Fc as shown in Scheme S3.

Step 3 : Again, the steady-current at high positive potential indicates the constant $C_{Fe2+,surface}$.

We assumed that all immobilized ferrocene is oxidized to Fc^+ , then

$$\frac{\partial C_{Fe2+,surface}}{\partial t} = -k_{cross} \Gamma_{FCSAM} C_{Fe2+,surface} + D_{Fe2+} \frac{(C_{Fe2+,bulk} - C_{Fe2+,surface})}{d} = 0$$

$$\leftrightarrow C_{Fe2+,surface} = \frac{D_{Fe2+} C_{Fe2+,bulk}}{d(k_{cross} \Gamma_{FCSAM} + \frac{D_{Fe2+}}{d})} \quad (\text{Eq. S4})$$

By combining eq. S3 and S4, it will give us

$$i = \frac{FAD_{Fe^{2+}}}{d} (C_{Fe^{2+},bulk} - C_{Fe^{2+},surface}) = \frac{FAD_{Fe^{2+}}C_{Fe^{2+},bulk}}{d} \left(\frac{dk_{cross}\Gamma_{FCSAM}}{dk_{cross}\Gamma_{FCSAM} + D_{Fe^{2+}}} \right)$$

$$i = \frac{FAD_{Fe^{2+}}C_{Fe^{2+},bulk}}{d} f(\Gamma_{FCSAM}), \quad f(\Gamma_{FCSAM}) = \left(\frac{dk_{cross}\Gamma_{FCSAM}}{dk_{cross}\Gamma_{FCSAM} + D_{Fe^{2+}}} \right) \text{ (Eq. S5).}$$

Equation S5 predicts the steady-state current under our experimental condition as following.

$$(D_{Fe^{2+}} = 7.6 \times 10^{-6} \text{ cm}^2/\text{s}, k_{cross} = 2.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}, \Gamma_{FCSAM} = 2.62 \times 10^{-11} \text{ mol/cm}^2, A = 1 \text{ cm}^2)$$

Gap distance(d, μm)	f	i (mA)
4	0.23	0.21
6	0.31	0.19
8	0.38	0.17

< **Table S1.** The predicted steady-state current based on equation S5. >

Origin of the leakage current in SAM-based electrochemical rectifier

To achieve high rectification ratio, it is very significant that SAM-based rectifier keeps the cathodic current small. There are two origin of cathodic current (or leakage current). One is simple charging current and the other is the faradic current of ferricyanide on SAM-modified/Au. In former case, the cathodic current might increase linearly with scan rate. In latter case, the current might increase linearly with concentration of redox species.

To prove which factor is dominant in our system, we performed CVs in electrolyte solution containing 1mM ferrocyanide at different scan rate, using three electrode system as shown in Figure S2. They showed that the cathodic current do not change dependent on scan rate, indicating minor contribution of charging current. On the other hand, Figure 3c shows CVs using two electrode configuration with different concentration of ferricyanide. The cathodic currents increase at higher concentration. Thus, we concluded that the dominant origin of cathodic current (leakage current) is the slow faradic current written in equation 3. Figure 3c also shows that the rectification ratio decrease by increase of C_0 concentration predicted by equation 4. (The increase of the leakage current is much higher than that of the forward-bias current at higher concentration.)

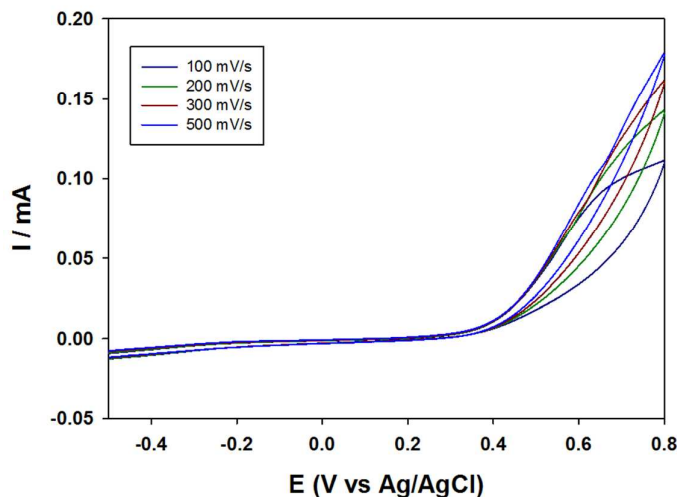


Figure S2. Three electrode I-V curves obtained in the electrolyte solution containing 1mM ferrocyanide at different scan rate. (100 mV/s ~ 500 mV/s)

Threshold potential in two terminal operation

Two terminal system doesn't have reference electrode such as Ag/AgCl so that the applied potential will distribute until the anodic current is exactly same to the cathodic current. Basically, the potentials of two electrode are floating. From half-cell reaction using three electrode configuration, however, threshold potential of ca. 0.2 V can be explained. Figure S3 showed the overlaid current density-potential behavior of each half cell reaction of our rectifier. To generate the same amount of anodic & cathodic current, ca. 0.2 V is necessary.

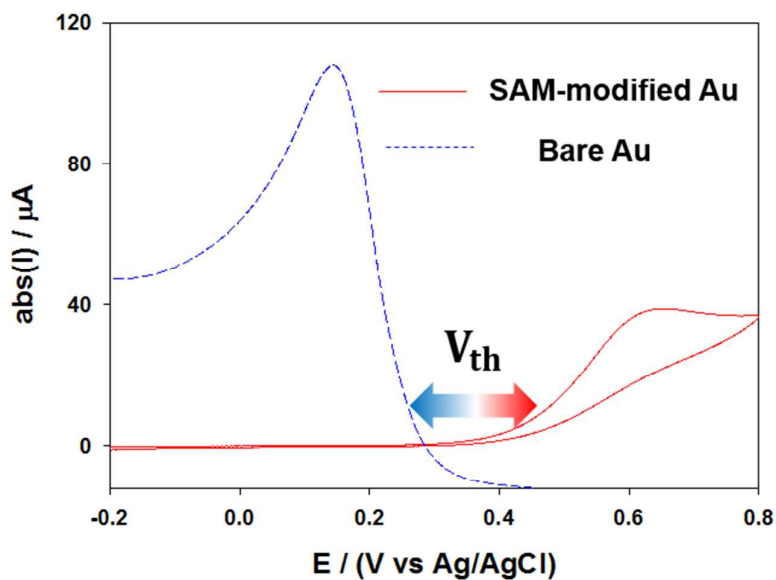


Figure S3. Overlaid current density-potential behavior for SAM-modified Au (anode) and Bare Au (cathode).

Formal potential of immobilized ferrocene.

Formal potential of immobilized ferrocene in Figure 1(A) is higher than that in previous reports. Several factors can affect the standard reduction potential of immobilized ferrocene on Au, including anions and distance between neighboring ferrocene. Among them, the degree of exposure of ferrocene to electrolyte also affect the E_0 . When binary SAM of hexadecanethiol (HDT, C16) and ferrocenyl-undecanethiol (C11) are formed on Au for our experiment, ferrocene moiety are surrounded by tall HDT. Namely, ferrocene is buried in long hydrophobic alkanethiols. Thus, the oxidation of ferrocene concomitant with pairing with counter anion becomes more difficult requiring the overpotential (shifted to more positive value) to oxidize Fc embedded into hydrophobic environment as previously reported.¹ (see Ref. 40 in the manuscript) When non-buried SAM of Fc was formed, CV showed typical E_0 values of ferrocene. In our rectifier, the mixed SAM composition (Fc embedded in long chain alkanethiol) was intentionally selected to block the leakage current at reverse bias.

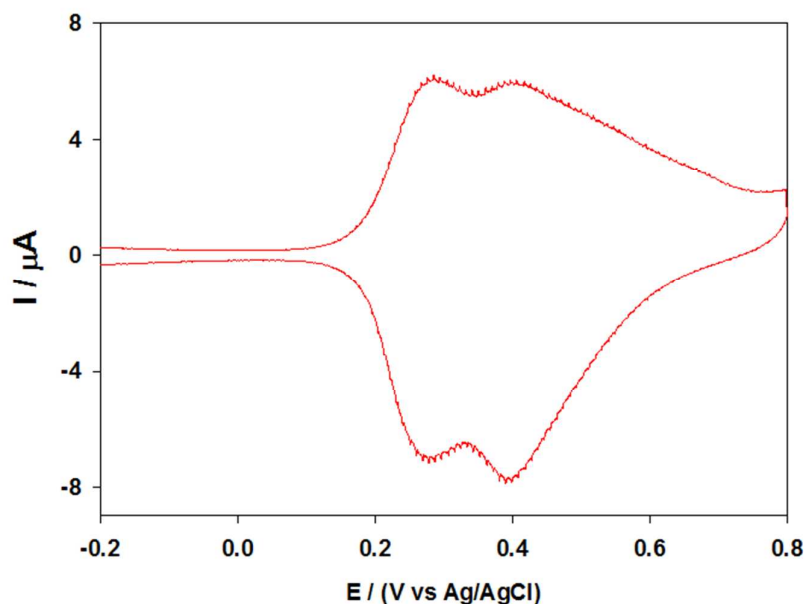


Figure S4. Non-buried Fc-UDT SAM CV in the electrolyte (scan rate= 50 mV/s).

Blocking behavior of mixed SAM

The electrochemical rectification relies on both the fast charge transfer to ferrocene and the blocking of oxidation of ferrocyanide on SAM. Thus, the well-ordered SAM is essential for electrochemical rectifier. We compare the electrochemical behaviors of various SAMs, (1) ferrocenyl dendrimer (FC-Den), (2) Fc-UDT SAM, and (3) mixed SAM of Fc-UDT and HDT. Except (3), other SAMs cannot block the charge transfer of ferrocyanide as shown in Figure S5. Overall, the quality of SAM (mixed SAM of Fc-UDT/HDT) is significant in electrochemical rectifier, which blocks the direct charge transfer of ferrocyanide with fast charge transfer to ferrocene.

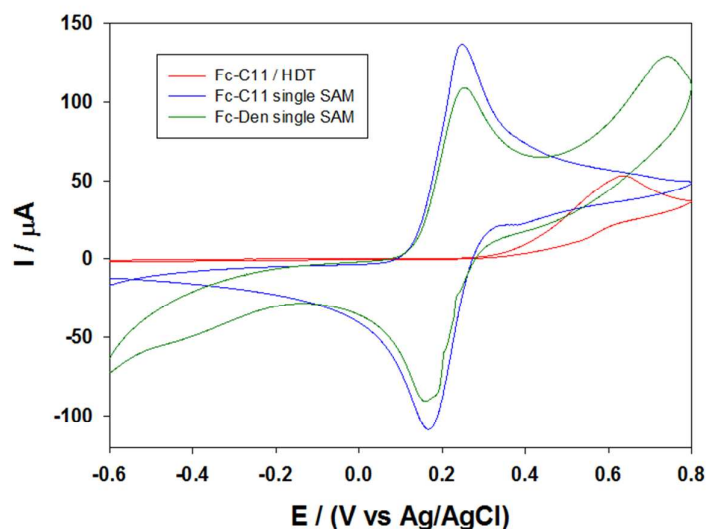


Figure S5. The comparison of leakage current from different composition Fc-SAMs. Single SAM dipped in 1mM Fc-undecanethiol or Fc-dendrimer thiol. Mixed SAM dipped in 1mM Fc-undecanethiol with hexadecanethiol.

References

- (1) Rowe, G. K.; Creager, S. E. Redox and Ion-Pairing Thermodynamics in Self-Assembled Monolayers. *Langmuir* **1991**, 7, 2307-2312.