

ADVANCED MATERIALS

Supporting Information

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An Aqueous Analog MAC Machine

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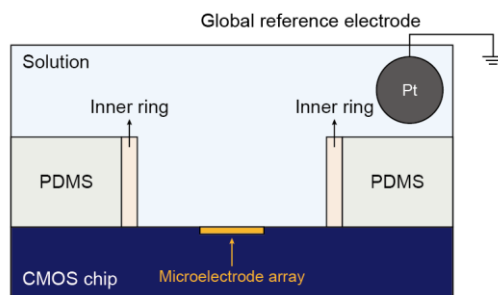


Figure S1. Experimental setup. The 16×16 ionic transistor array on the CMOS chip is exposed to the aqueous solution, while other areas of the chip are covered by PDMS. The system employs a Pt electrode as a global reference electrode.

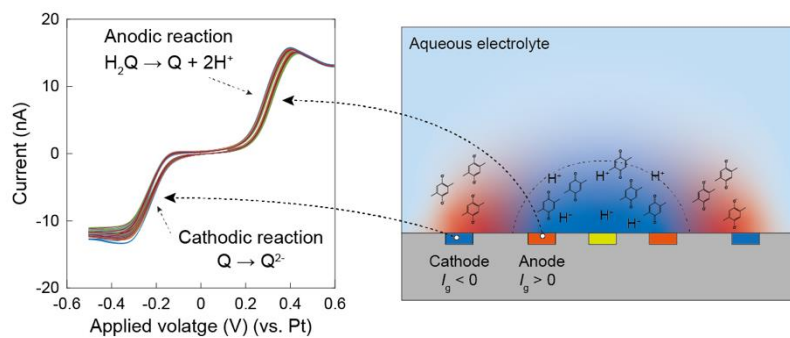


Figure S2. Quinone electrochemistry. (Left) Cyclic voltammetry (CV) in a solution containing 20 mM H_2Q and 5 mM Q identifies the redox reactions of the quinone redox couple. (Right) The concentric ring pair utilizes these redox reactions to localize $[H^+]$ and $[Q]$ above around the pixel center.

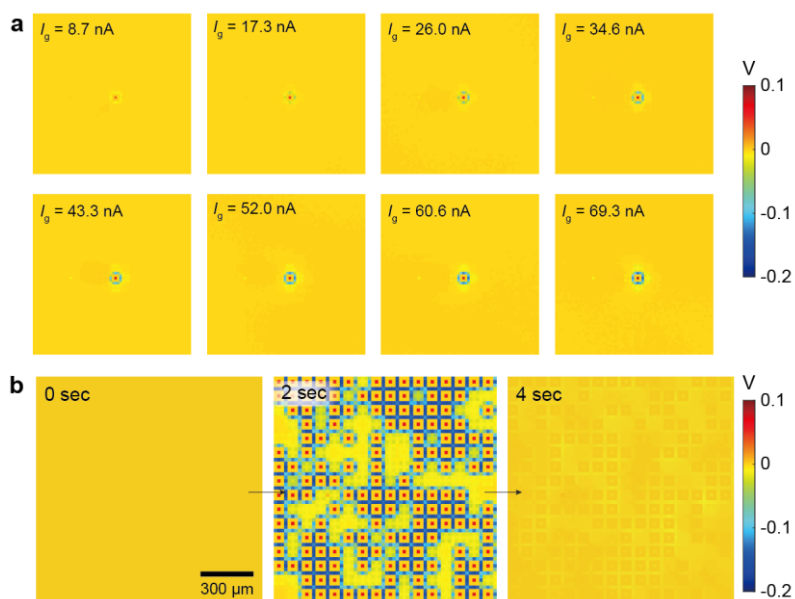


Figure S3. Electrolytic concentration localization (as part of the review of Ref. [11]). (a)

A single pixel is activated with different I_g values. The measured OCP is increased at the pixel center and decreased outside the pixel, *i.e.*, the pH at the pixel center is decreased, and the pH outside the pixel is increased. The OCP difference between the pixel center and outside the pixel increases with I_g . **(b) Figure 1f** of the main text showed that the local electrolytic concentration control can be achieved simultaneously at any set of pixels we choose to activate. The present figure above is another experiment of the same essence, but with a different set of pixels we chose to activate ($I_g = 52.0$ nA).

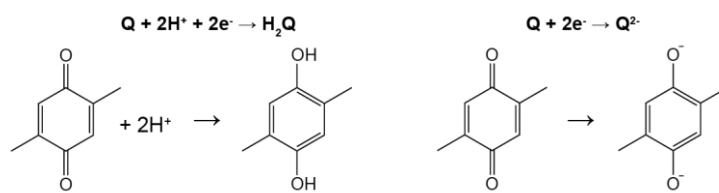


Figure S4. H^+ -assisted (left) vs. normal (right) reduction of quinone.

Supplementary note

Electrochemistry underlying Figures 2d and 2e

First consider the local $[Q]$ and $[H^+]$ above the pixel center with the I_g -gating but with no V_{in} applied yet. The I_g -gating raises them by Δ and 2Δ via the oxidation, $H_2Q \rightarrow Q + 2H^+ + 2e^-$, at the inner ring, with a larger I_g giving a larger Δ . *I.e.*, $[Q] = [Q]_0 + \Delta$ and $[H^+] = [H^+]_0 + 2\Delta$ ($[Q]_0$ and $[H^+]_0$ are the normal Q and H^+ concentrations). As the solution dissolves a good amount of Q and its preparation is nearly neutral, $[Q]_0 > \Delta$ and $\approx 10^{-7} \text{ M} \ll 2\Delta$ for any practical I_g . Thus, overall, $[Q] = [Q]_0 + \Delta$, $[H^+] \approx 2\Delta$, and $[Q] > [H^+]$ with the I_g -gating.

With these local $[Q]$ and $[H^+]$ set by the I_g -gating, we now explain I_{out} vs. V_{in} at the center disk seen in **Figures 2d** and **2e**. In Region A with small $|V_{in}|$ (**Figure 2d**), only the H^+ -assisted reduction ($Q + 2H^+ + 2e^- \rightarrow H_2Q$) occurs at the disk. As this reduction is mild in Region A, it produces I_{out} that linearly increases with $|V_{in}|$, while not substantially changing the local $[Q]$ and $[H^+]$ set by the I_g -gating. Furthermore, since $[Q] > [H^+]$, I_{out} is dictated by $[H^+]$ instead of $[Q]$. Concretely, the slope $dI_{out}/d|V_{in}|$ is proportional to $[H^+] \approx 2\Delta$. Hence in Region A, a larger I_g (which yields a larger Δ) leads to a larger slope $dI_{out}/d|V_{in}|$, as seen in **Figure 2d**.

In Region B with larger $|V_{in}|$ (**Figure 2e**), both the H^+ -assisted reduction ($Q + 2H^+ + 2e^- \rightarrow H_2Q$) and normal reduction ($Q + 2e^- \rightarrow Q^{2-}$) occur at the disk. Let I_T and I_S be the currents from the H^+ -assisted and normal reductions ($I_{out} = I_T + I_S$). Since the H^+ -assisted reduction is strong and exhausts all H^+ ions at the disk surface for any V_{in} in Region B, I_T does not vary with V_{in} . This saturated I_T sets a baseline for I_{out} . For a larger I_g and thus a larger Δ , more H^+ ions, originating from $[H^+] \approx 2\Delta$ with the I_g -gating, are exhausted at the disk surface. Hence, a larger I_g produces a larger I_T , or a larger baseline for I_{out} . Now, as the H^+ -assisted reduction exhausts H^+ ions at the disk surface, driving $[H^+] \approx 2\Delta$ down to $[H^+] \approx 0$ at the disk surface, it drives down $[Q]$ from $[Q]_0 + \Delta$ to $[Q]_0$ at the disk surface. This remaining $[Q]_0$ at the disk surface is the reactant of the normal reduction. As the normal reduction is mild in Region B, I_S linearly increases with $|V_{in}|$, with the slope $dI_S/d|V_{in}|$ proportional to $[Q]_0$. As $[Q]_0$ is independent of I_g , the slope $dI_S/d|V_{in}|$ does not vary with I_g . Putting all of above together with $I_{out} = I_T + I_S$, we see that the baseline of I_{out} (*i.e.*, I_T) increases with I_g , which corresponds to the intercept T of I_{out} decreasing with I_g , and that the slope $dI_{out}/d|V_{in}|$, which is identical to the slope $dI_S/d|V_{in}|$, is independent of I_g . These are consistent with **Figure 2e**.

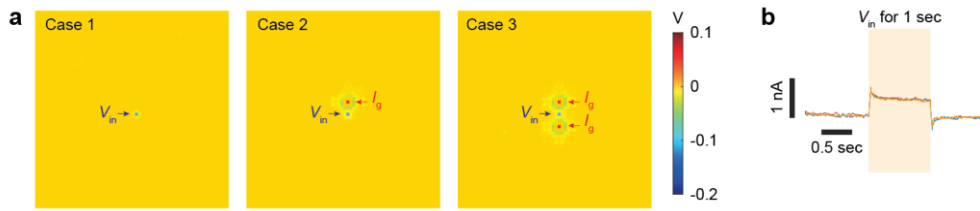


Figure S5. Additional interference testing. (a) In each of the three cases shown, we apply a V_{in} pulse (amplitude: -0.08 V) to pixel 9 of a column, and measure the resulting I_{out} . We always set $I_g = 0$ for the chosen pixel. In Case 1, $I_g = 0$ for all rest fifteen pixels in the column. In Case 2, $I_g = 26.0$ nA for one neighboring pixel (pixel 8) in the column while $I_g = 0$ for the remaining fourteen pixels in the column. In Case 3, $I_g = 26.0$ nA for both neighboring pixels (pixel 8 and 10) in the column while $I_g = 0$ for the remaining thirteen pixels in the column. (b) The measured I_{out} 's for the three cases are nearly identical, showing again that the localized environment for a given transistor is effective only for that transistor, and hardly interferes with other transistors.



Figure S6. Another additional interference testing. (a) For Case 1 and 2, we apply a V_{in} pulse (amplitude = -0.08 V) to only pixel 9 and only pixel 8 (which belong to the same column), respectively. For Case 3, we apply the same V_{in} pulse (amplitude = -0.08 V) to both pixel 9 and pixel 8 simultaneously. $I_g = 0$ for all pixels for all three cases. (b) The measured I_{out} 's for Case 1 and Case 2 are nearly identical and the measured I_{out} for Case 3 is the same as the sum of I_{out} 's for Case 1 and Case 2. This shows that the two activated center disks with $I_g = 0$ do not interfere with each other.

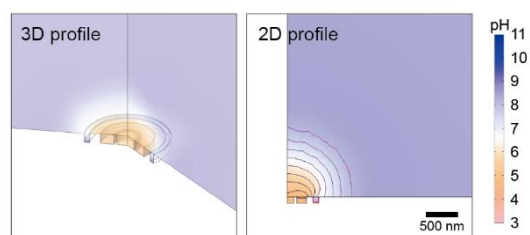


Figure S7. Simulated sub-micrometer scale pH localization. In COMSOL simulation of a scaled-down pixel, with the diameters of the outer and inner rings being 600 nm and 900 nm, we still obtain [Q] and [H⁺] localization, now with $I_g = 64$ pA (the size scaling leads to the smaller I_g for the concentration localization), where the [H⁺] localization is shown here in the form of pH.