

Supporting Information

Electronic paper by plasmonic electrochromic active matrix

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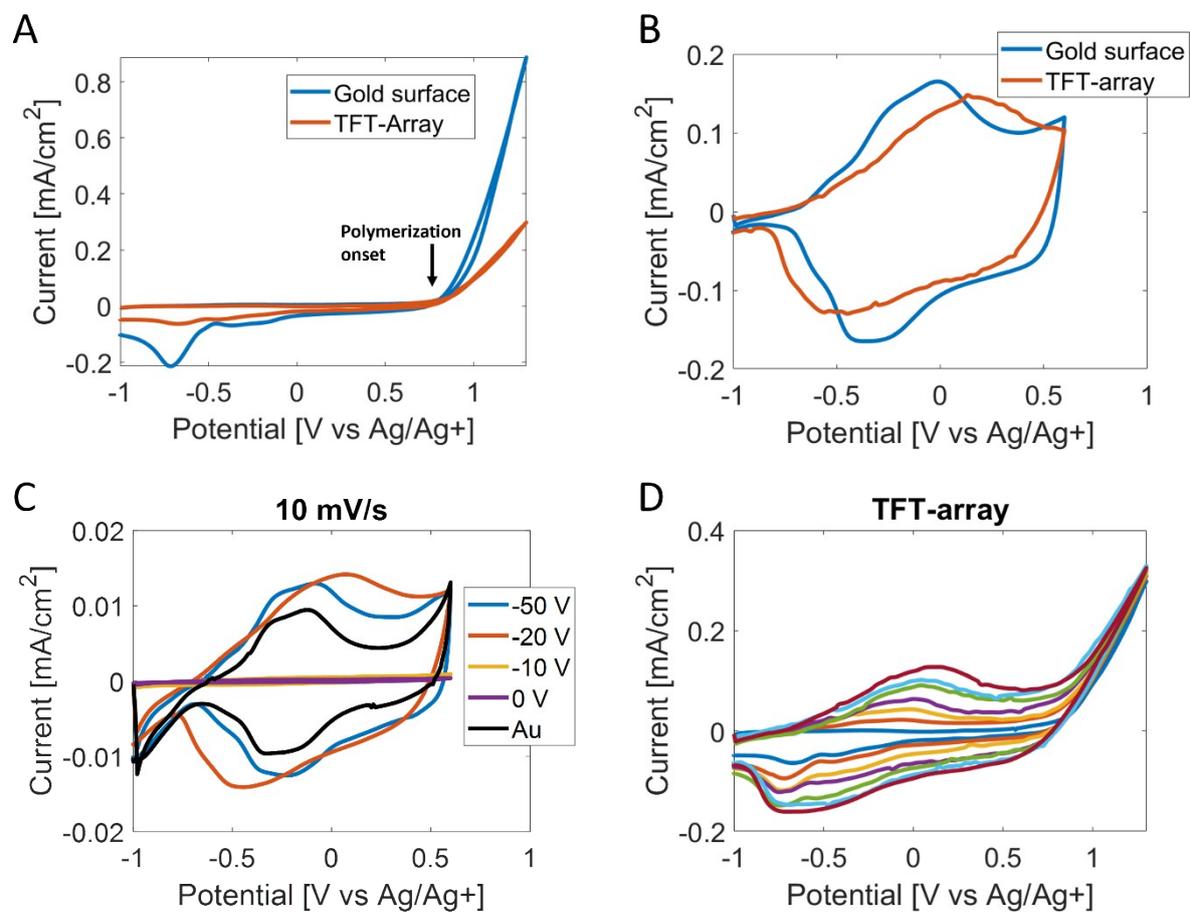
Additional electrochemical data

Figure S1 A) Polymerization of PProDOT-Me₂ on a bare gold surface and on the TFT array. B) Cyclic voltammetry (100 mV/s) of PProDOT-Me₂ on a bare gold surface and on the TFT array (V_g = -50V). C) Cyclic voltammetry (10 mV/s) on a bare gold surface and on the TFT array with various gate voltages. D) Polymerization with cyclic voltammetry on TFT array.

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Driving circuit

To realize a functioning electronic paper, a driver circuit has to be present to automatically update the image. Even though electrochromic devices can be used in a 2-electrode configuration, we decided to build a driver that utilized a three-electrode setup. This increased the complexity of the circuitry but opened for more accurate potential control of each pixel. This configuration extends the TFT array beyond electronic paper to be able to function as a highly multiplexed electrode for various electrochemical experiments. A potentiostat was built on a breadboard [1] where the working electrode was multiplexed to three different source lines. The two gate lines were opened by additional MOSFETs. A schematic of the driver can be seen in Figure S2A where, from right to left, an Arduino operates the MOSFETs, switching between -40 V (from the power supply) and +2.5 V. The potentiostat's working electrode is grounded (+2.5 V) and fed into a multiplex. When a potential (-1 V \rightarrow +0.4 V vs. Ag/Ag⁺) is applied to the potentiostat's counter electrode adjusts its potential until the voltage across the working and reference is as desired. An image of 6×2 bundled pixels was updated by sweeping through the pixels. Video recordings (SI) show the image switching that occurs when different pulse times are tried. One trial shows each pixel updating one at a time with a period of around 1 second. The second trial shows a shorter gate pulse time (~ 0.25 sec) which gives a more uniform switch of the image. A rudimentary image and its inverted version can be seen in Figure S2B and C.

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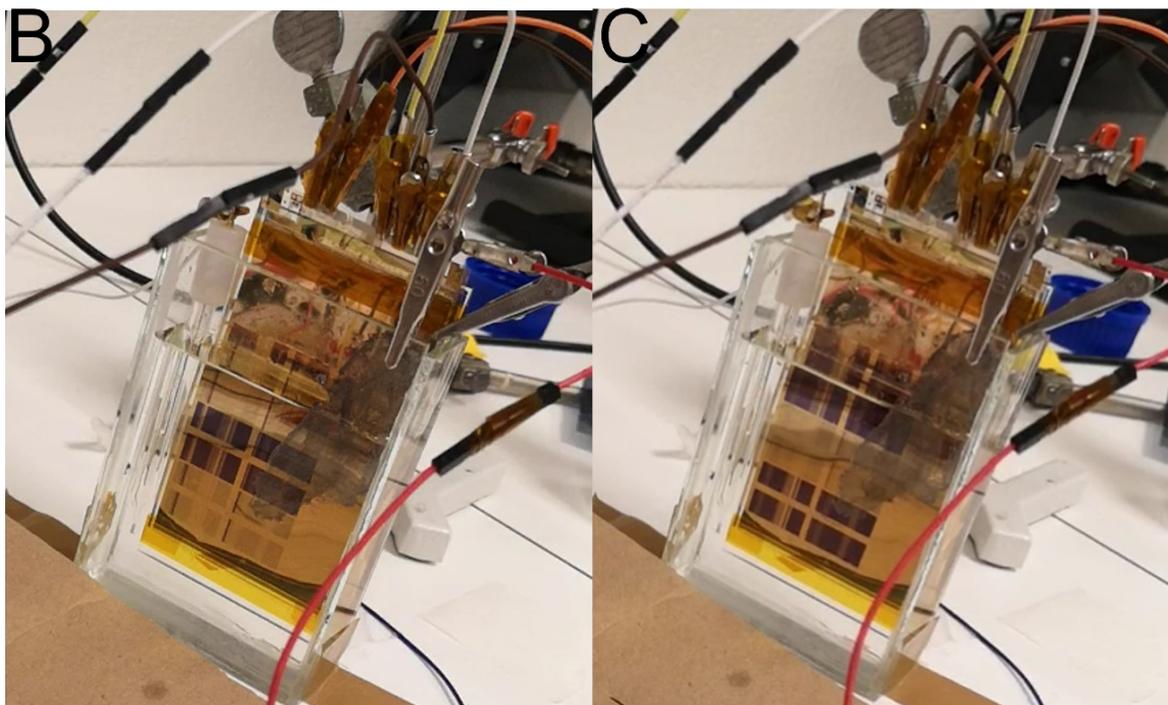
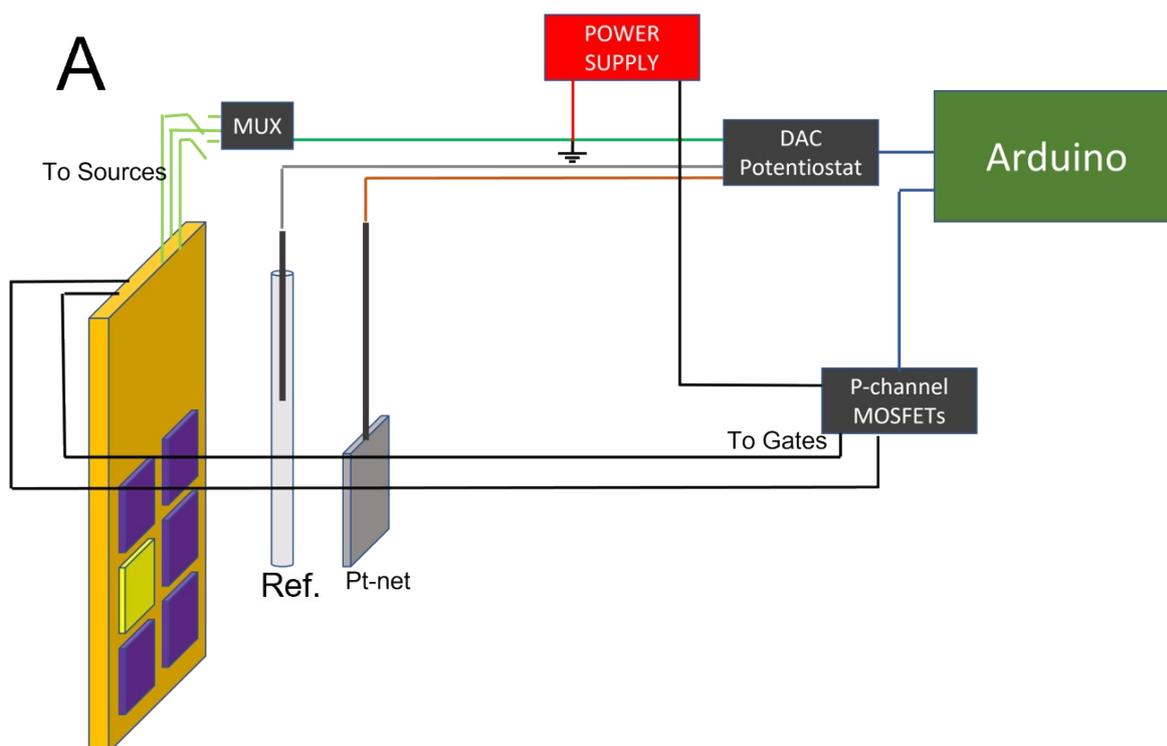


Figure S2 A) Schematic of driver for a multiplexed potentiostat. B) Pixel banded together to form 2x3 matrix where the middle row is turned to colored state. The rows are source lines (connected to the potentiostat) and the columns are gate lines (connected to open and closing the transistors).

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Storage capacitor

To retain the applied voltage on the pixels while the row is unselected, a pixel capacitor is incorporated to "hold" the voltage while other rows are updated. This storage capacitor is built-in the backplane and has one terminal connected to the source while the other terminal leads to a fan-out terminal (the fan-out terminal is the same for all storage capacitors). The capacitors can be engaged by connecting the fanout terminal to the counter electrode. To understand if the built-in storage capacitor of the TFTs can be charged up and further inject charge into the polymer after the gate is closed, and no more current passes from the potentiostat, the built-in storage capacitor is connected parallel to the electrochromic material (between the working and counter). Figure S3A shows a schematic where now a 2-electrode configuration is used (Pt-counter is reference and counter). We found that there was no difference in switching time between the 2 and 3 -electrode configurations when using potentials -1V and +0.6 V (Figure S3B). The switching time on a gold substrate of a polymer of a similar thickness is 0.6 seconds (Figure S3B). For the TFT array, the switching time is ~ 1.4 seconds for both dark to bright, and bright to dark. The higher switching time can be attributed to the residual resistance in the TFT. When utilizing the built-in pixel capacitor, no difference in switching time was observed (Figure S3C). Unexpectedly, the bistability was diminished when connecting the pixel capacitor compared to leaving it unconnected (Figure S3D). This suggests that the pixel capacitor discharges the electrochromic material instead of keeping the voltage. As a final trial to engage the storage capacitor the magnitude of the applied voltage was increased. For a bright-to-dark switch, the initial potential was + 0.6 V and the potential for reaching the dark state was -1 V, -2 V, -5 V, or -10 V. The gates were put in an open state ($V_G = 0$ V, no current flow) and closed ($V_G = -50$ V, current allowed) in pulses of 100 ms every 10 seconds (arrows in Figure S3D). This effectively pulses the polymer with a very high voltage in pulse times of 100 ms. If the storage capacitor would be engaged, and have a sufficient capacitance for switching the

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polymer, the reflection would further decrease after the 100 ms pulse had been released. An additional contrast would come from the injected current from the capacitor. This is not what is observed, and the contrast is only occurring during the 100 ms switch (Figure S3E). However, due to the high voltage, the switch times can be decreased. If -2 V is used, 5 pulses of 100 ms are required for a full bright-to-dark switch. 2 pulses are required for -5 V and 1-2 pulses for -10 V. When decreasing the pulse time to 10 ms and using -10 V, 10 pulses were required to reach full contrast and there was little to no difference between connecting, or disconnecting, the pixel capacitor (Figure S2F).

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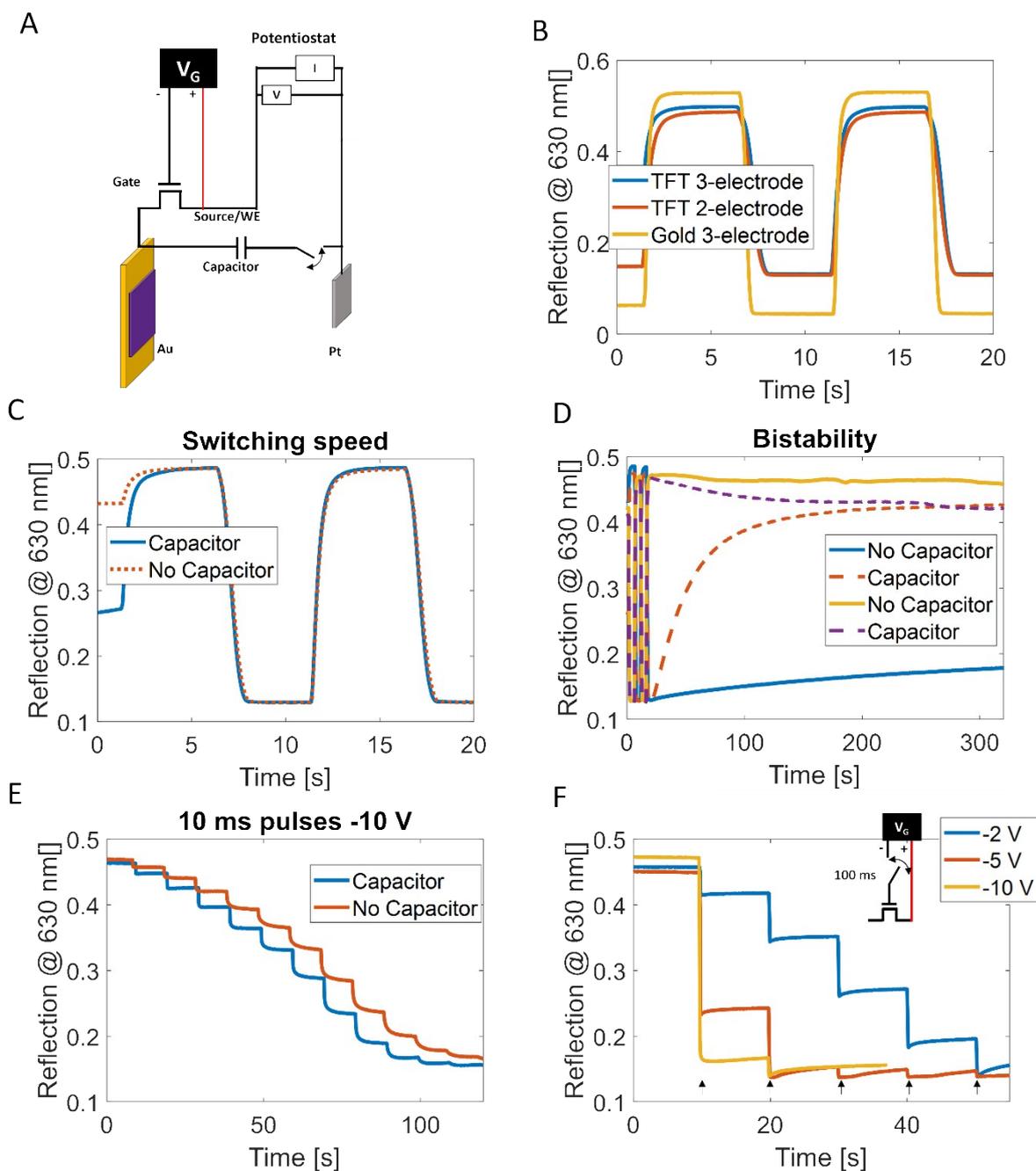


Figure S3 A) Schematic of setup with pixel capacitor included B) Switching of TFT in 2 or 3-electrode setup gave similar switching time. C) Switching speed with and without the pixel capacitor connected to the counter electrode D) Bistability with (- -) or without (-) the capacitor connected. E) Constant potential of -2 V, -5 V, or -10 V with the gates closed for 100 ms pulses every 10 seconds (arrows). B) Using the storage capacitor with high voltage pulses did not show a significant reduction in switching time with higher applied voltages.

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Wire bonding

Due to the non-rigidity of the substrate and the fine pitch of the fan out, wire bonding was very difficult and the yield of high-quality bonds without any short circuits was low. To increase rigidity, the TFT was taped onto a custom-made printed circuit board (PCB) (Figure S4A). The bonds extended from the TFT to gold lines on the PCB where the potentiostat could be easily connected. A microscope image of the bonds can be viewed in Figure S1B. To increase the yield of successfully bonded connections, multiple sources or gates from the fan-out were bonded to the same PCB connection. This generated multiple patterns of squares of polymers on the backplanes. However, far from every “square” is perfect due to non-proper connections (Figure S4C). A schematic of how the wire bonding can be seen in Figure S4D.

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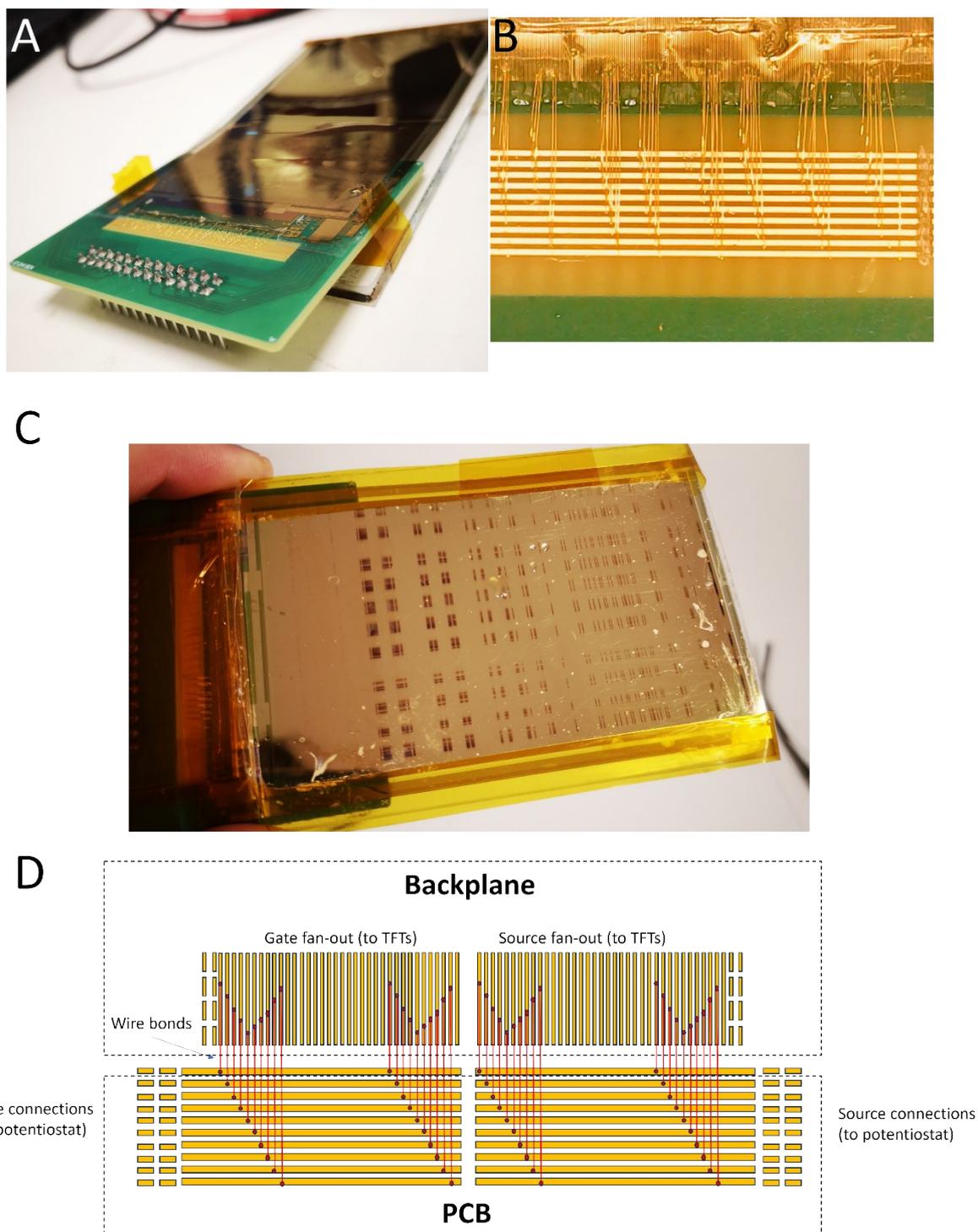


Figure S4 A) The TFT backplane on the PCB with wire bonds. B) Microscope image of some of the wire bonds. C) Multiple "squares" of polymer generated on a backplane. D) Schematic of wire bonds.

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- [1] G. N. Meloni, "Building a Microcontroller Based Potentiostat: A Inexpensive and Versatile Platform for Teaching Electrochemistry and Instrumentation," *Journal of Chemical Education*, vol. 93, no. 7, pp. 1320-1322, 2016, doi: 10.1021/acs.jchemed.5b00961.