Supporting information

Bipolar Electrode Arrays for Chemical Imaging and Multiplexed Sensing

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Device fabrication. The electrode patterns were formed on a 3-inch glass wafer by a thin-film process. To form the platinum BPEs, chromium (50 nm thick) and platinum (150 nm thick) were deposited onto patterns of a positive photoresist (S1818G) using a sputtering machine (CFS-4EP-LL, Shibaura Mechatronics, Yokohama, Japan). Chromium served as an intermediate layer to promote adhesion of the platinum layer. The metals on the photoresist were lifted off by immersing the glass wafer in acetone, resulting in the BPE patterns. The wafer was rinsed well in fresh acetone and dried by blowing dry nitrogen gas. To form the gold BPEs, chromium (50 nm thick) and gold (200 nm thick) were first sputter-deposited onto a cleaned glass substrate. After electrode patterns were formed on the gold layer with the positive photoresist, the exposed gold areas were chemically etched in a solution containing 600 mM potassium iodide and 200 mM iodine. After removing the photoresist in acetone and rinsing the wafer well in fresh acetone, the wafer was immersed in a solution containing 3.1 M NaOH and 800 mM $K_3[Fe(CN)_6]$ to remove exposed chromium, using the gold patterns as a protective layer. The wafer was rinsed well with pure water and dried by blowing nitrogen gas to obtain the gold BPEs. Following the standard process recommended by the manufacturer, surfaces of both the platinum and gold BPEs were insulated with a polyimide layer, leaving the contact pads and the anodic and cathodic poles of the BPEs exposed. Finally, the chips were cut out from the wafer using a dicing machine (A-WD-10A, Tokyo Seimitsu, Tokyo, Japan). The dimensions of the chips were 20 mm × 50 mm.

Reaction chambers to accommodate the cathodic and anodic poles were formed with polydimethylsiloxane (PDMS). For this purpose, a mold was formed with poly(methyl methacrylate) (PMMA) using a laser engraver (Rayjet-50, Trotec Laser GmbH, Marchtrenk, Austria). Two 13 mm × 13 mm × 5 mm PMMA blocks were made using the engraver, and these blocks were adhered together using acetone to create a 10-mm-thick block. Two pieces of these blocks were further adhered to a 5 mm-thick PMMA plate, along with another 46 mm × 34 mm PMMA frame that surrounded the blocks to create a reservoir for holding the prepolymer solution. The prepolymer solution of PDMS and the corresponding curing agent were mixed in a weight ratio of 10:1, put in a vacuum chamber, and the chamber was evacuated to remove air bubbles from the mixture. The mixture was then uniformly poured into the PMMA mold to the top without covering the top surface. After curing for 30 min at 80°C, the PDMS was peeled off from the mold. The planar dimensions of the formed chambers were 13 mm × 13 mm and the depth was 10 mm. PDMS flow channels (Figure S3) for the surface modification of BPEs and DNA detection were formed in the same manner, using patterns of a thick-film photoresist (SU-8 25, Kayaku Advanced Materials, Westborough, MA) as a mold (100 μm thick). The standard procedure was followed to form the SU-8 mold.

Measurement of lead resistances. The resistances of the leads connected to the cathodic and anodic poles were measured using a digital multimeter (2407A, B&K Precision, Yorba Linda, CA).

Table S1. Length and resistance of the shortest and longest leads in type I and II devices.

	Type I				Type II	
	4 × 5 array		6 × 8 array		9 × 10 array	
	Shortest leads	Longest leads	Shortest leads	Longest leads	Shortest leads	Longest leads
Length (mm)	5.7	22.5	6.7	21.5	6.1	22.5
Resistance (Ω)	66.8 (2.4)	258.0 (1.9)	95.0 (2.7)	299.6 (3.7)	89.2 (1.7)	322.9 (7.1)

Resistance was measured for 5, 8, and 10 leads for the 4 × 5, 6 × 8, and 9 × 10 arrays, respectively, and the averages and standard deviations (within the parentheses) were as shown.

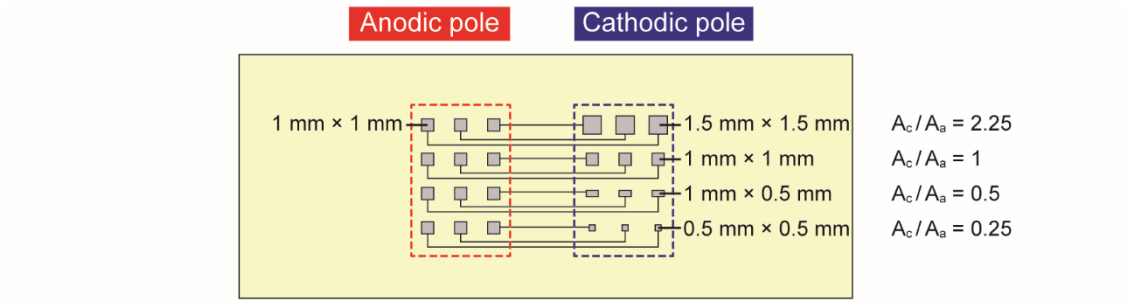

Figure S1. BPEs with cathodic and anodic poles in different area ratios.

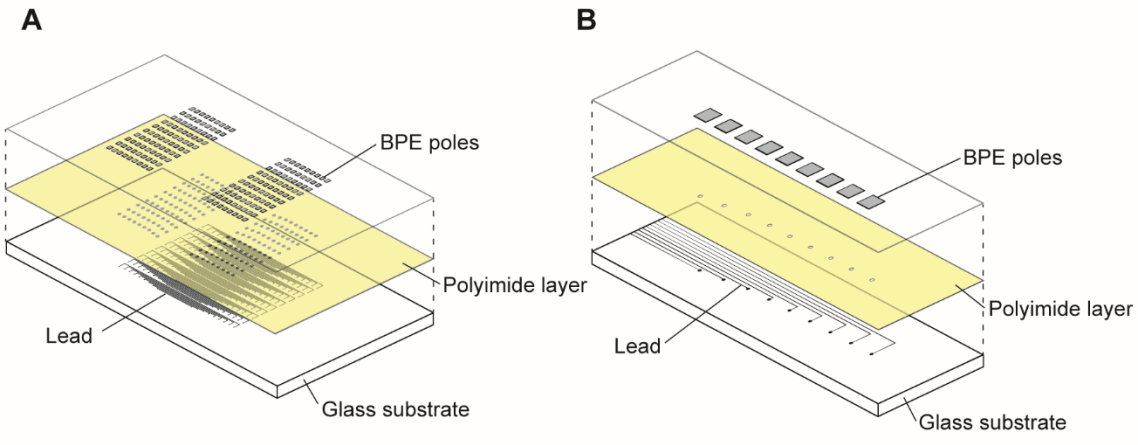

Figure S2. Magnified views of the type II device, including the leads on the glass substrate, polyimide insulating layer with areas open to contact, and the cathodes and anodes. (A) Magnified view of the entire chip. (B) Magnified view of the part around one of the cathode arrays.

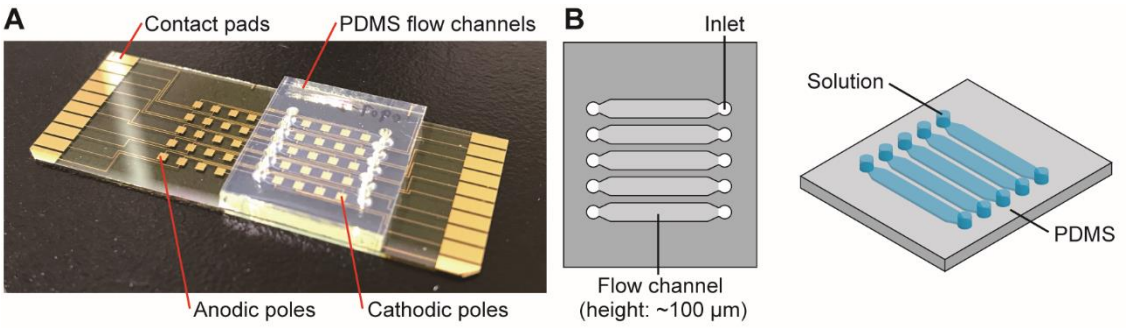

Figure S3. Device with gold BPEs and PDMS flow channels used for modifying the cathodic poles and detecting DNAs. (A) PDMS substrate with five flow channels attached to the cathodic side of the BPEs. DNA solutions were injected into the flow channels. (B) Top view and 3D figure of the PDMS flow channels containing injected solutions.

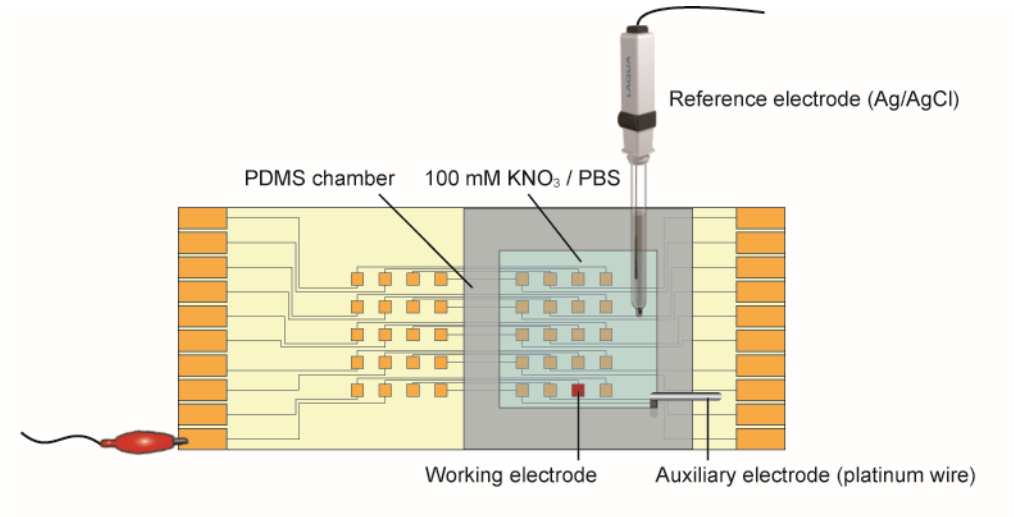

Figure S4. Setup of the three-electrode system.

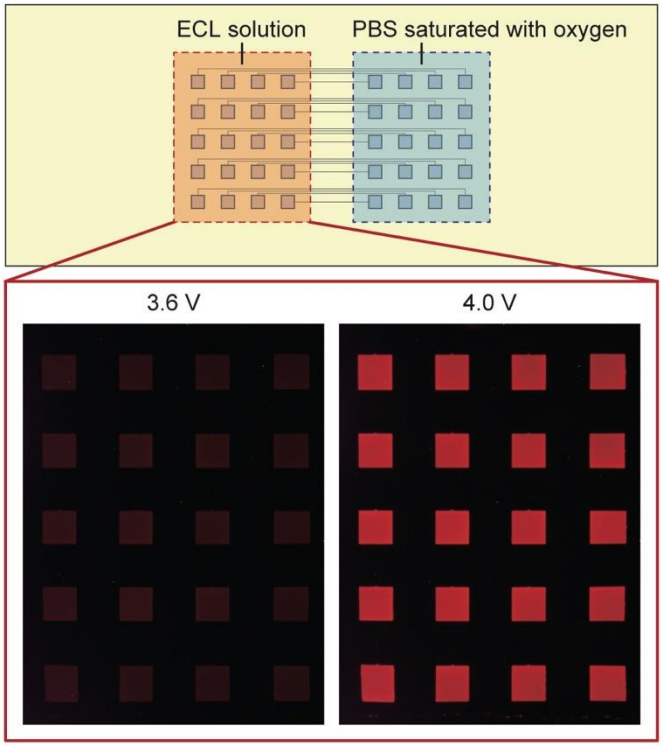

Figure S5. ECL from the array of platinum anodic poles at the driving voltages of 3.6 and 4.0 V. The sensing chamber was filled with PBS (pH 7.4) containing 100 mM KNO_3 and saturated with air. Dimensions of the cathodic and anodic poles were 1.0 mm × 1.0 mm.

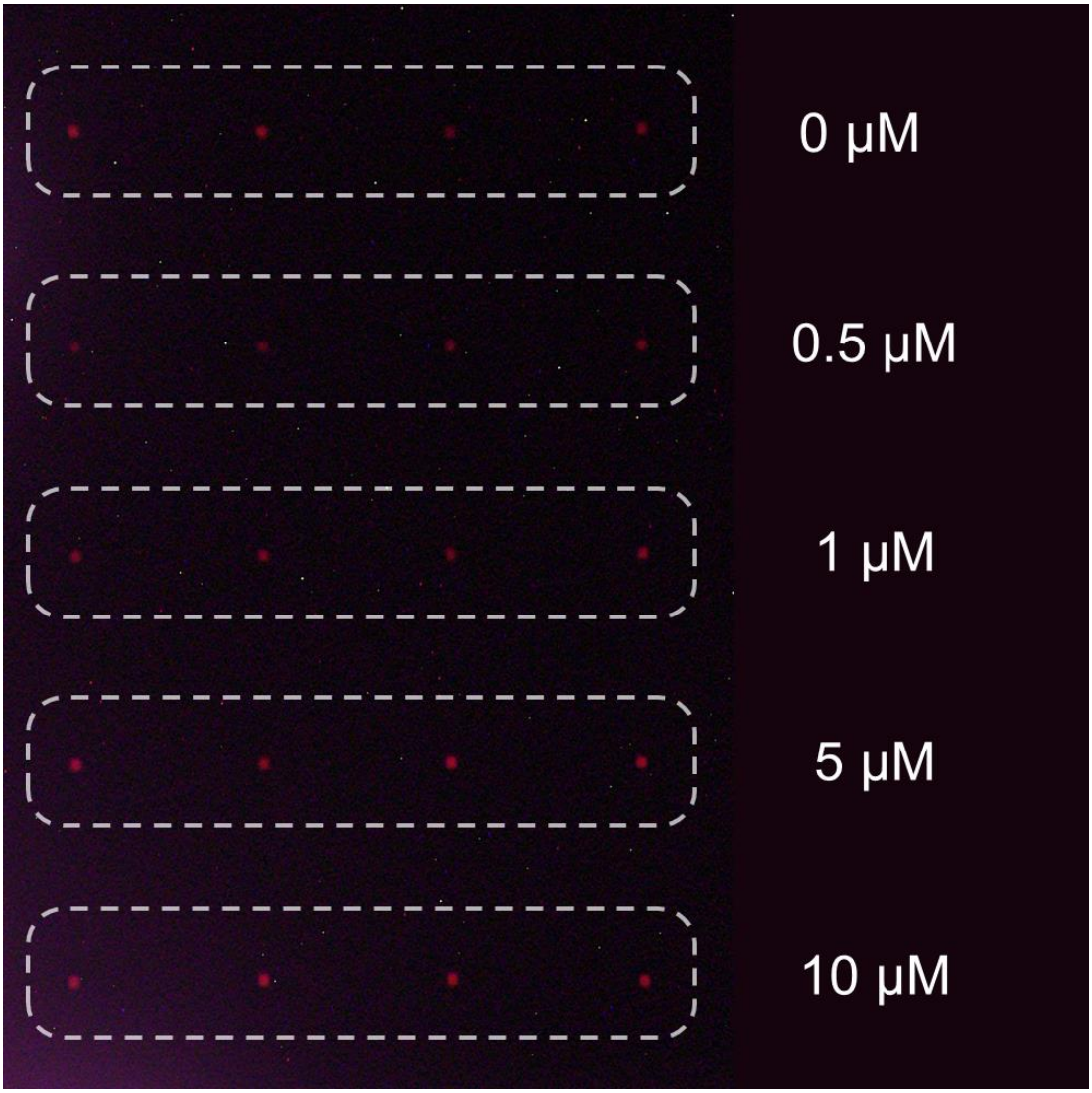

Figure S6. Magnified version of the ECL images in Figure 8B.