SUPPLEMENTARY MATERIALS FOR:

Highly-efficient biocompatible single silicon nanowire electrodes with functional biological pore channels

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1. **Materials and Methods**

Silicon Nanowires Synthesis: P-type silicon nanowires electrodes were produced by the chemical deposition following previously described method.[1] Briefly, 30-nm colloidal gold nanoparticles (Ted Pella) were deposited onto a silicon substrate that was previously functionalized with poly L-Lysine (0.1% aqueous solution, Ted Pella). After deposition, the substrate was rinsed with DI water (18 MΩ-cm), dry with N_2, and cleaned with oxygen plasma to remove organic materials. Silicon nanowires synthesis was carried out in a 1-inch quartz tube furnace at 460 ºC using 5 sccm of SiH_4 (10% in He, Voltaix) and 25 sccm of B_2H_6 (100ppm in He, Voltaix) for 2 hours. Once the synthesis was completed, the resulting SiNWs were suspended in solution by 5 second sonication in ethanol. TEM images of the SiNWs were recorded with a Phillips CM300 FEG TEM operated at 300 KV and equipped with a Gatan imaging filter system.

Devices Fabrication: Silicon Nanowires were deposited by flow alignment onto a silicon substrate (1-10 MΩ-cm) with 250 nm thick dry oxide grown at 1200ºC. Metal contacts to the SiNWE were defined by photolithography followed by e-beam deposition of 20 nm of Ti and 80 nm of Pt. 80 nm of PECVD stoichiometric silicon nitride were subsequently deposited to conformally passivate the metal contacts in a Semigroup 1000TC operating at 100ºC, 300mTorr, and 14 Watts with silane and ammonia as source gases. The devices were placed in a liftoff solution bath for 4 hours, water rinsed, and dried in a convection oven for 2 hours at 125 °C. Prepared SiNWE devices were then coated with a 400 nm thick layer of LOR-3A (MicroChem), baked at 180 °C for 5 minutes, and coated again with a layer of photoresist. Rectangular openings 5-7 μm wide and 30 μm long were patterned by photolithography exposing the SiNWE surfaces, but not the nitride coated metal contacts. Finally, the substrate was rinsed with acetone, so the photoresist was completely removed leaving the LOR-3A layer on the surface. The resulting net dielectric stack of 400 nm LOR-3A and 80 nm PECVD Si_3N_4 ensures that the electrochemical studies are carried out at the surface of the SiNWE and not at the metal contacts.

Cyclic Voltammetry System Set Up: Potentials were swept against a leakage free Ag/AgCl (3 M KCl) reference electrode (Warner Instruments) by steps of 5 mV for 1 second or 6 mV for 3 seconds from 0 to 0.6 V with a source meter (Keithley 2602) in a similar configuration as previously reported.[2] SiNWEs were enclosed in a PDMS channel and exposed to a solution of either 100 mM KCl + 5 mM potassium-PBS, pH = 7 buffer, or to potassium ferrocyanide in the same buffer with concentrations of 10 mM (multiple SiNWE) or 50 mM (single SiNWE and flat silicon electrodes). Reagents were purchased from Sigma-Aldrich with purity 99.9 % or better.

Elipsometry. A Rudolph Research ellipsometer equipped with a 632.8nm laser at a fixed angle of 70° was used to estimate the thickness of oxide layer for flat electrodes. The refractive index of the silicon oxide was assumed to be equal to 1.46.

Lipid Vesicle Preparation, Supported Bilayer Formation, and α-Hemolysin Incubation: Unilamellar vesicles of DOPC lipid were prepared by sonication of a solution of 2 mg/ml 1,2-Dioleoyl-sn-glycero-3-phosphocholine (DOPC, Avanti Polar Lipids) in buffer. After voltammetric studies of the silicon electrodes, the reference electrode was removed and vesicles solution introduced into the PDMS chamber. Vesicle fusion onto SiNWE and flat silicon electrode was allowed for approximately. 24 hours followed by a rinse with buffer, and a final rinse with redox solution constantly avoiding any introduction of air bubbles. Finally, the reference electrode was placed again into the PDMS chamber. Once the voltammetric characterization of lipid coated devices is finished, the PDMS chamber was rinsed with buffer and then incubated with 100 μg/ml α-Hemolysin (Sigma-Aldrich) in buffer between 18 to 24 hours.[3] Linear and nonlinear regression of experimental voltammetric data for bare, bilayer coated, and α-HL incubated samples were performed with IGOR Pro 5.02(WaveMetrics, Inc).

2. **Electrochemical Characterization of Flat Silicon electrodes**

Flat silicon electrodes were fabricated from heavily doped p-type (100) single-side polished wafer (0.002-0.005 Ω·cm). Square silicon chips were immersed in buffered HF with surfactant for 30 seconds, rinsed with DI water, and immediately placed in an E-beam evaporator unit to deposit 20 nm of Ti followed by 80 nm of Pt on the unpolished side at a pressure of 10^{-7} Torr. Once the deposition was completed, a PDMS channel was placed onto the polished side to form a fluid cell for electrochemical studies.

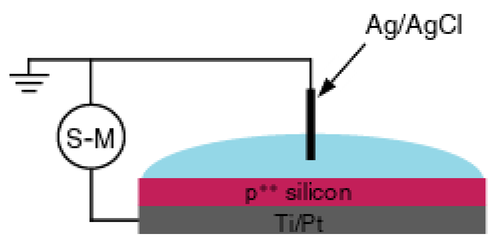

Figure S1. Experimental configuration used for characterization of flat silicon electrodes.

The electrochemical characterization of the flat silicon electrodes, supported lipid bilayers, and α-hemolysin incubated samples followed the procedures described for silicon nanowire electrode characterization. Figure S3A shows a characteristic voltammetric response for bare and DOPC bilayer coated flat silicon electrode. The exponential dependence of the faradic current with respect to the applied potential is an indication that experimental data can be modeled with the Tafel equation (Eq. 3 in the manuscript).[4]

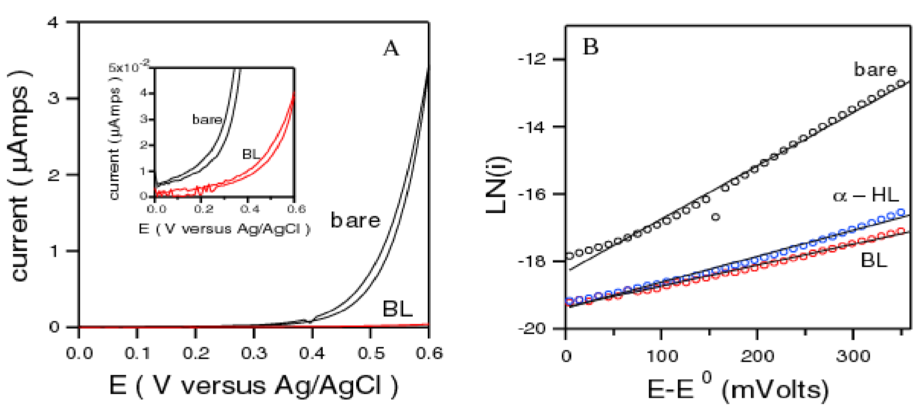

Figure S2. (A) Faradic current response versus applied voltage for bare and DOPC bilayer (BL) coated electrode. Inset is a magnification of the BL response. (B) Tafel plot for bare, BL, and α-HL. Solid lines are the Tafel equation fitting for the experimental data. Area of the electrode was 0.5cm^2

References

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