Supporting Information

Higher Sensitivity Dopamine Measurements with Faster-Scan Cyclic Voltammetry

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Supplemental Data Analysis Methods. Quantization noise was calculated as follows. First, an electrode was cycled with the 1.0 V waveform at 400 V/s. Next, an average of three digital background-subtracted cyclic voltammograms without the presence of analyte was calculated without filtering or smoothing. The standard deviation of the resulting cyclic voltammogram was taken as a noise level. Finally, the scan rate was increased in 400 V/s increments up to 2400

V/s and the procedure was repeated. Signal-to-noise ratios were calculated by analyzing peak current versus time traces. A low frequency polynomial was used to fit a baseline to remove drift and signal to noise ratios were determined by dividing the maximal response by the standard deviation of 1 s of noise. The effect of the time constant of the current-to-voltage converter was evaluated by convolution as described elsewhere.[S1]

ABS utilization for faster-scan cyclic voltammetry. Figure S-1 illustrates how analog background subtraction (ABS) was used to enable faster-scan cyclic voltammetry. When the carbon-fiber microelectrode was scanned faster, a larger charging current was generated. A digitized version of background charging current measured at 400 V/s was fed into the summing point of the current-to-voltage converter, neutralizing some of the measured charging current, preventing the analog to digital converter from reaching saturation.

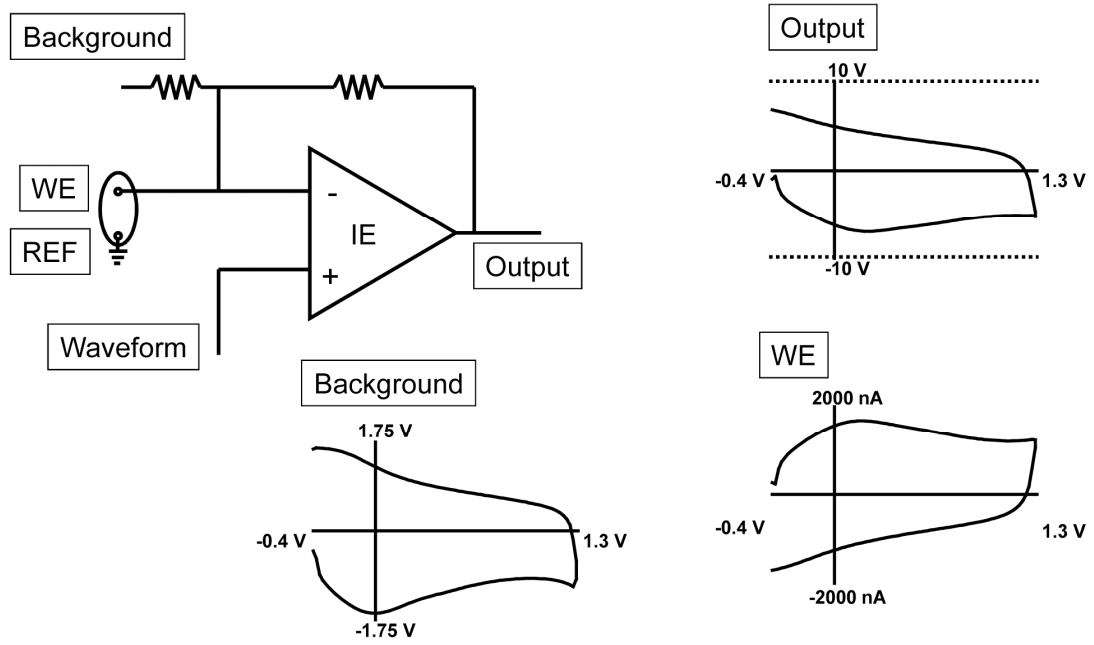

Figure S-1. ABS utilization for faster-scan cyclic voltammetry. WE represents the carbon-fiber microelectrode and REF represents the Ag/AgCl reference electrode. The dotted lines of the output represent saturation of the analog-to-digital converter used for the measurement.

Calibration of the 1.0 V waveform. Figure S-2 shows absolute peak current as a function of scan rate for 1 μM dopamine in vitro with the 1.0 V waveform.

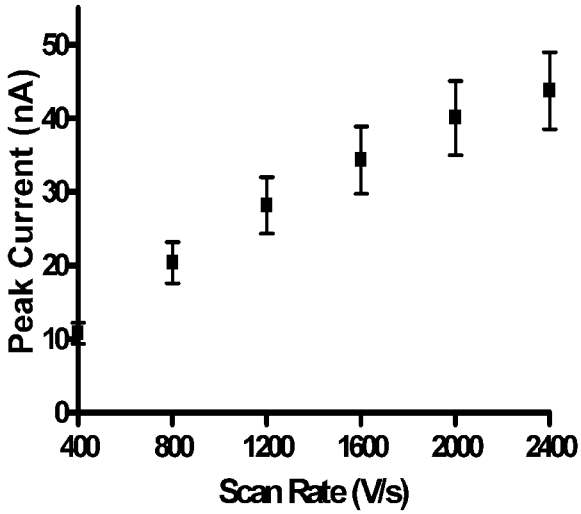

Figure S-2. Dopamine (1 μM) peak current versus scan rate for the 1.0 V waveform in vitro. N = 5 electrodes.

Temporal comparison of the 1.3 V voltammetric excursions. Figure S-3 compares the duration and shapes of the 1.3 V cyclic waveform at 400 V/s (A), the 1.3 V cyclic waveform at 2400 V/s (B), and the 1.3 V sawhorse waveform at 2400 V/s (C).

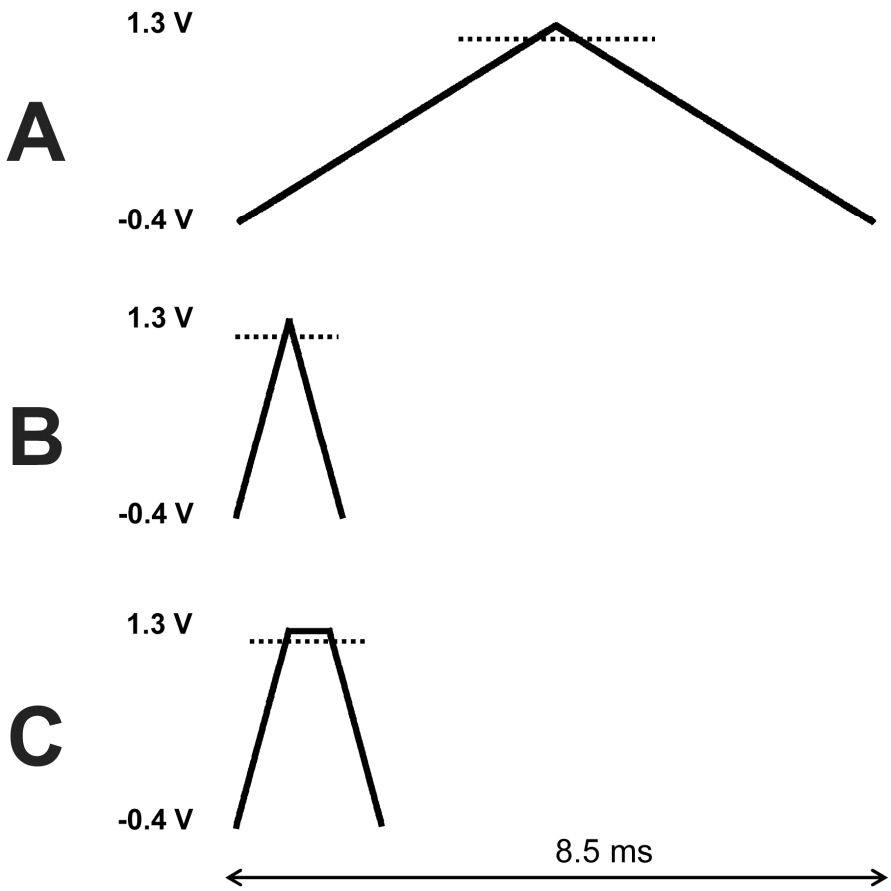

Figure S-3. 1.3 V excursions versus time for the 1.3 V cyclic waveform at 400 V/s (A), the 1.3 V cyclic waveform at 2400 V/s (B), and the 1.3 V sawhorse waveform at 2400 V/s waveform (C). The horizontal dotted line represents 1.0 V.

Environmental scanning electron microscopy. The procedure was adapted from previous work.[S2] Carbon-fiber microelectrodes were imaged before and after waveform application. Microelectrodes were rinsed with copious quantity of DI water to remove residual salt. A total of 6.48×10^6 cycles of a selected waveform was applied to a carbon-fiber microelectrode as done previously[S2] in PBS buffer, pH 7.4. Electrical connection with the carbon-fiber microelectrode was made using a stainless steel wire and a silver-based paint (GC Electronics, Rockford, IL); backfill solution was not used to prevent evaporation in the instrument. Because the duration of each voltammetric excursion differed, each waveform was applied at a different frequency such that all waveforms had 6.5 ms of holding time between sweeps. Images were collected using

FEI Quanta 200 FEG environmental scanning electron microscope (FEI Company, Hillsboro, OR) in low-vacuum mode with electron beam energy of 13 kEV and at magnifications of 1.5 k, 3 k and 10 k. Diameters were estimated using ImageJ.[S3] Etch rates were calculated by subtracting the final diameter from the initial diameter, dividing by the number of waveform cycles, and multiplying the result by 1000 to produce a chemically appropriate result. Representative environmental scanning electron microscopy images after the application of each waveform are shown in Figure S-4.

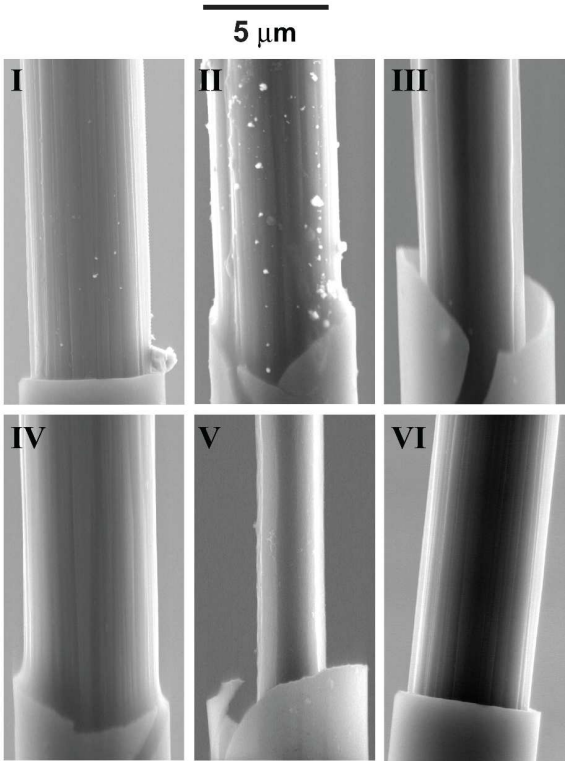

Figure S4. Carbon-fiber microelectrode etching as a function of the applied waveform. A) Representative ESEM images of a carbon-fiber microelectrode (I) after the 1.0 V waveform at 400 V/s, (II) after the 1.0 V waveform at 2400 V/s, (III) after the 1.3 V cyclic waveform at 400 V/s, (IV) after the 1.3 V cyclic waveform at 2400 V/s, and (V) after the 1.3 V sawhorse waveform at 2400 V/s. A carbon-fiber microelectrode before waveform application is shown for comparison (VI).

References

(1) Wipf, D. O.; Kristensen, E. W.; Deakin, M. R.; Wightman, R. M. *Anal. Chem.* **1988**, *60*, 306-310.

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(3) Rasband, W. S.; U.S. National Institutes of Health: Bethesda, Maryland, USA, http://rsb.info.nih.gov/ij/, 1997-2009.