Supplementary Information:

High Young's Modulus Carbon Fibers Are Fouling Resistant with Fast-Scan Cyclic Voltammetry

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METHODS

Chemical reagents

Dopamine (DA), 5-Hydroxytryptamine (5-HT) and 5-Hydoxyundole acetic acid (5-HIAA) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Stock solutions were stored in 0.1 M HCl (Fisher Scientific). Daily solutions were diluted from stock in pH 7.4 Tris buffer. Tris buffer includes 15 mM Tris, 1.25 mM NaH_2PO_4, 2.0 mM Na_2SO_4, 3.25 mM KCl, 140 mM NaCl, 1.2 mM $CaCl_2$ dehydrate, and 1.2 mM $MgCl_2$. All solutions were made from deionized water (Milli-Q, Millipore, Billerica MA).

Fast-scan cyclic voltammetry experiments: Fast-scan cyclic voltammograms were collected using the WaveNeuro potentiostat with a 5 megaohm headstage (Pine Instruments, Durham NC) and data was collected using HDCV software (UNC-Chapel Hill, Mark Wightman). A potential waveform was applied to the electrode against a Ag/AgCl reference electrode. A home-built flow injection analysis system was used to deliver a small bolus of analyte at the electrode at a flow rate of 1 mL/min using a Fusion 200 Two-Channel Chemyx syringe pump (Stafford, TX). Electrodes were allowed to equilibrate for 10 min prior to experimentation. For the calibration curve, the “serotonin waveform” was used for 5-HT and 5-HIAA on TS30 electrodes to minimize fouling at the traditional carbon-fiber and to facilitate a direct comparison in sensitivity between the traditional method of serotonin detection to the high modulus fibers at a more traditional waveform. The serotonin waveform scans from 0.2 V to 1.0 V, down to -0.1 V and scan back to 0.2 V at 1000 V/s and frequency of 10 Hz. The “traditional waveform” was applied to the high modulus fibers for constructing calibration curves for 5-HT and 5-HIAA and scans from -0.4 V to 1.3 V and back at 400 V/s and frequency of 10 Hz. The traditional waveform was used for all calibrations involving dopamine. The concentrations tested for the calibration curve include 1 μM, 3 μM, 5 μM, 7 μM, and 10 μM. The fouling experiments were all conducted at the traditional

waveform. Due to rapid scan rates, all nonfaradaic charging current was removed through background subtraction.

Carbon-fiber microelectrode fabrication: Cylindrical carbon-fiber microelectrodes were fabricated as described previously[1] from 7-µm TS30 carbon fibers, 6-µm MS40, and 5-µm HS40 carbon fiber (Mitsubishi Chemical Carbon Fiber and Composites Inc., Sacramento CA). Carbon-fibers were vacuum aspirated into a glass capillary with dimensions 1.2 x 0.68 mm (A&M Systems, Sequim WA). Glass capillaries were pulled using a Narishige PE-22 Electrode Puller (Tokyo, Japan). Carbon-fibers were cut 50-100 µm in length under a microscope. All electrodes were soaked in isopropyl alcohol for at least 10 minutes prior to use and backfilled with 1M KCl.

Carbon nanotube (CNT)-fiber microelectrode fabrication: The CNT-fiber electrodes were fabricated as previously described.[2] Briefly, a glass capillary with dimensions 1.2 x 0.68 mm was pulled into two using a Narishige PE-22 Electrode puller. The tapered end of the glass was cut under a microscope to approximately 50 µm and a single 15-µm in diameter CNT-fiber was pulled through the opening. The electrode was sealed with Epon Resin 828 (Miller-Stephenson, Danbury, CT) and cured with 14 % (w/w) 1,3-phenylenediamine hardener (Sigma Aldrich). Further curing of the electrode seal was completed in an oven set to 150º C overnight. The disk electrode was polished to a 45º angle (Sutter Instrument model BV-10, Novato, CA).

Electroactive surface area estimation: The estimated electroactive surface area of each of the fibers was calculated using the Randles-Sevcik equation (Equation 1). The surface area was calculated based on the average current detected for 1 µM dopamine for each of the 3 fiber types. (TS30 = 43.7 ± 5.8 nA, MS40 = 8.98 ± 2.2 nA, and HS40 is 6.20 ± 1.1 nA). The diffusion coefficient

for dopamine is well established with FSCV (6.0 x 10^{-6} cm^2/s) and was used in this calculation.[3] The scan rate (v) is equal to 400 V/s and n = 2.

$$i_p = (2.69\ x\ 10^5) n^{\frac{3}{2}} A D_0^{\frac{1}{2}} C_0^* v^{\frac{1}{2}} \qquad (1)$$

Surface characterization experiments: Scanning electron microscopy (SEM) was taken using a FEI XL30 SEM. Images were collected at an accelerating voltage of 2.00 kV, 5-6 mm away. Raman spectra was collected of the sides of the carbon fibers using a Renishaw InVia Raman microscope (Guocestershire, UK) excited by a 633 nm Ar-ion laser at 10 % power. The D/G ratios were calculated by taking the area under the curve of the "D" or disorder peak and dividing it by the area under the curve of the "G" or graphitic peak, like previously reported.[2]

Statistics: All statistics were performed in GraphPad Prism 8 (GraphPad Software Inc., La Jolla CA). Statistical p values were considered significant at the 95% confidence interval. Values reported are mean ± standard error of the mean (SEM) with *n* representative of the number of electrodes.

Supplemental References:

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3 B. J. Venton, K. P. Troyer and R. M. Wightman, *Anal.Chem.*, 2002, **74**, 539–546.