Supplementary Material for

Cavity Carbon Nanopipette Electrodes for Dopamine Detection

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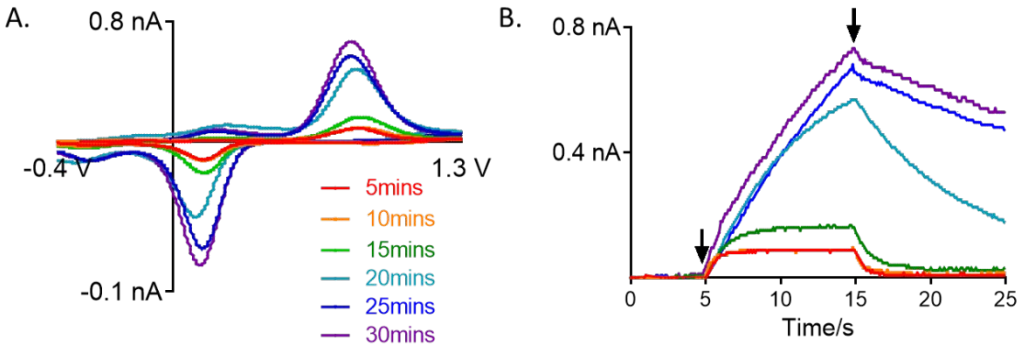


Figure S1. Electrochemical response to 1 μM dopamine at an open tube CNPE. Measurements were obtained at scan rate of 400 V/s and scan repetition frequency of 10 Hz for 30 mins with the measurement interval of 5 mins. (A) Background subtracted cyclic voltammogram to 1 μM dopamine, and (B) measured oxidation current versus time for a flow injection analysis experiment (dopamine bolus injection and changing back to PBS buffer are marked as black arrows).

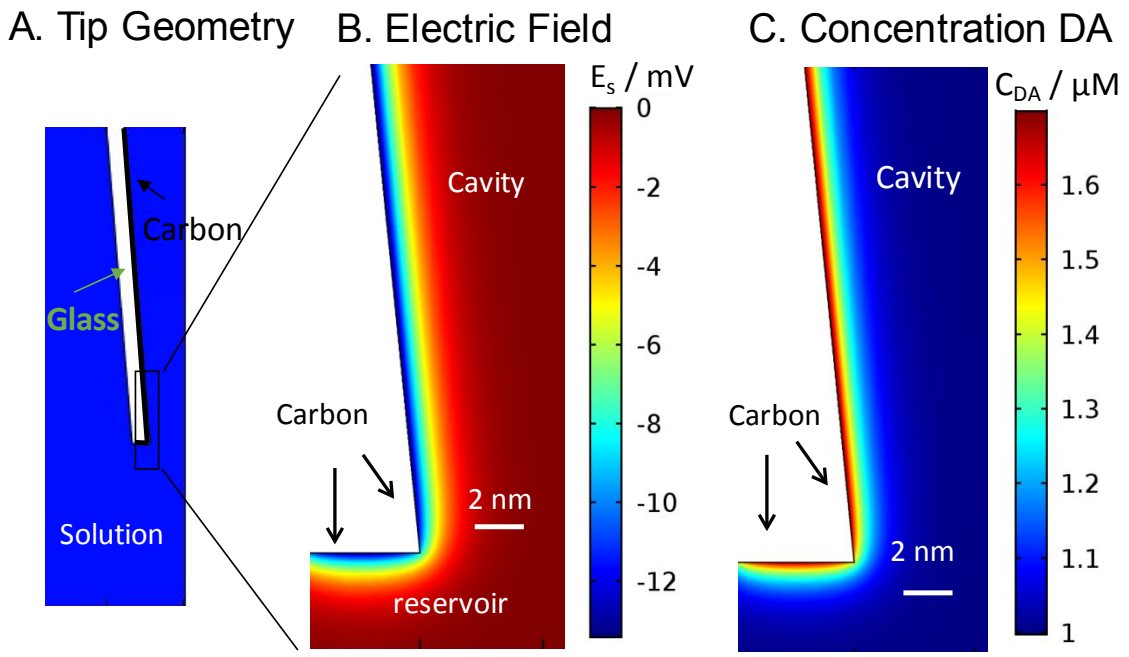


Figure S2. Numerical simulations of double layer and preconcentration. A. Diagram showing the tip geometry. Double layer simulations are enlarged at the tip. B. Electric field/double layer simulation. The electric field is larger, but negative, at the carbon surface. C. Concentration of dopamine is enhanced at the surface due to the electric field. All conditions are at steady state. E_{app} = 0 V, Surface charge density = -0.01 C/m^2, a = 200 nm, C_{DA} = 1 µM.

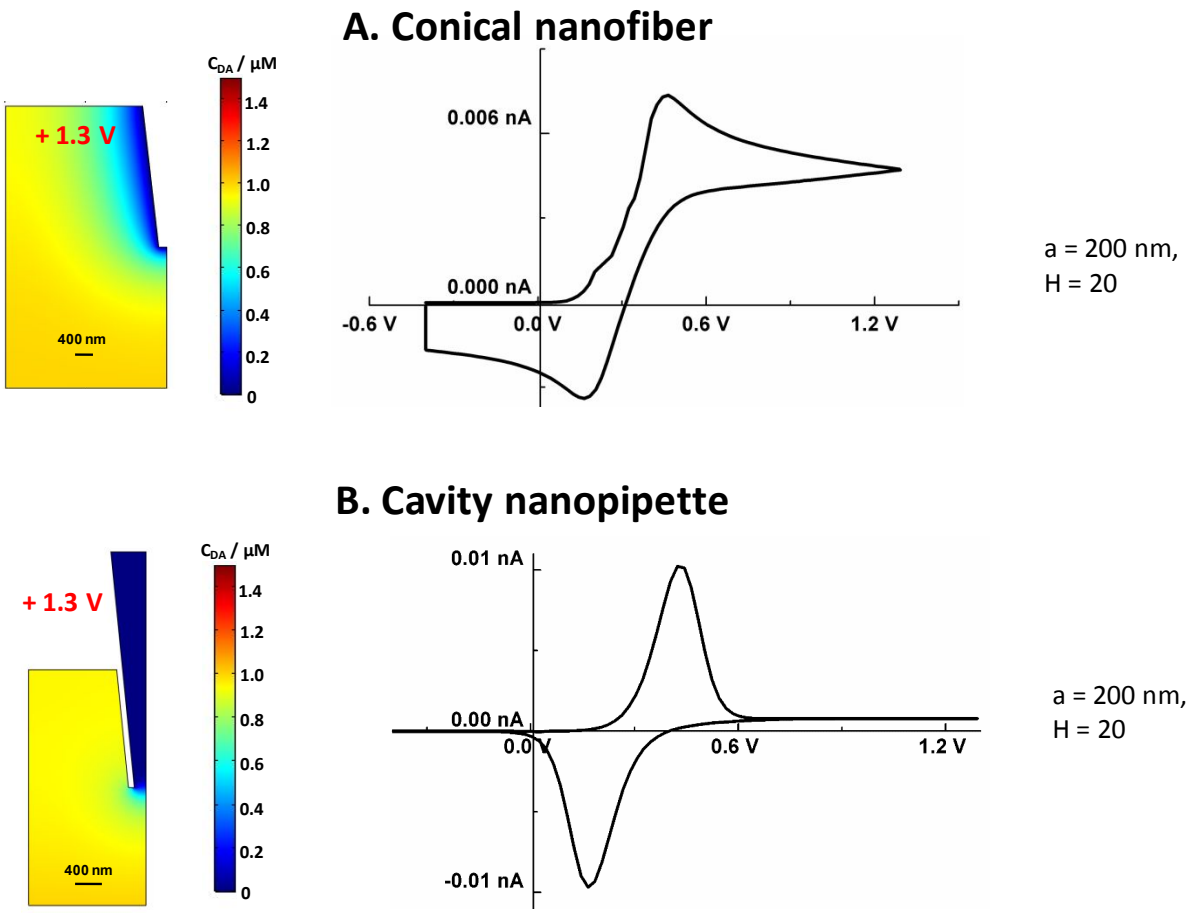
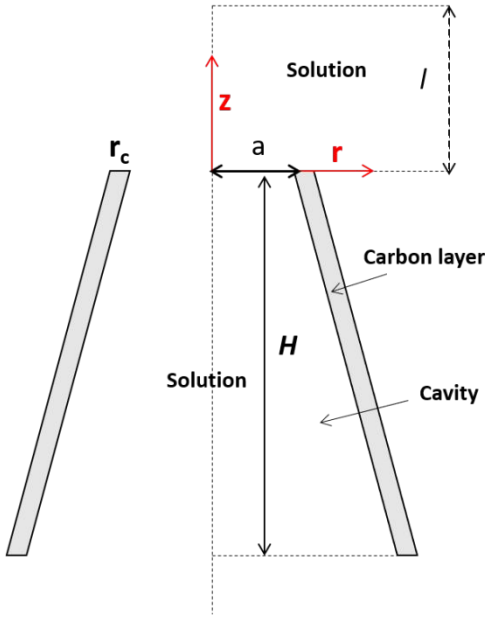


Figure S3. Comparison of currents at (A) conical nanofiber electrode and (B) cavity nanopipette. The expected currents for 1 µM dopamine are 30 % higher at the nanopipette electrode because of the trapping and redox cycling. Geometry of each pipette was the same, with a=200 and H=20.

Supplemental Methods

Finite element simulation of cavity carbon nanopipettes (CNPES) for dopamine detection

Finite-element analysis of the dopamine oxidation/reduction in carbon nanopipettes was conducted using COMSOL Multiphysics 5.3a. A 2D-axisymmetric model (Scheme S1) was used to describe the electrochemical features of the dopamine in the cavity nanopipette with the carbon-coated inner wall. The variables ***z*** and ***r*** refer to the coordinates perpendicular and parallel to the carbon nanopipettes orifice, respectively. The geometric parameters *a*, r_c, *l*, θ, and *H* represent the pipette radius, carbon layer thickness, reservoir depth, pipette angle and the nanopipettes depth, respectively.



Scheme S1. The 2D axisymmetric simulation model and parameters for the cavity CNPES.

The "Transport of Diluted Species" and "Electrostatics" modules of COMSOL were coupled to simulate the electric double layer structure and electrochemical processes at the deposited carbon layer. The solution contains the reduced redox form R, the oxidized form O, the cation K^+ and the anion Cl^- as supporting electrolyte. Within the whole solution domain, including the cavity and outside bulk solution, the ionic transport flux, including diffusion and migration, in the solution

reservoirs and cavity carbon nanopipettes was described by the Nernst-Planck equation (S1), and the solution electric potential was calculated using the Poisson equation (S2):

$$J_i = -D_i \nabla c_i - \frac{z_i F}{RT} D_i \nabla c_i \nabla \phi \quad (0 \le r < r_s,\ H < z < l;) \qquad \text{(S1)}$$

$$\nabla^2(\varepsilon_0 \varepsilon_r \phi) = -F \sum_i z_i c_i \quad (0 \le r < r_s,\ H < z < l;) \qquad \text{(S2)}$$

where D_i, C_i, and z_i are the diffusion coefficient, concentration, and charge of the ionic species *i*, *F* is the Faraday constant, *R* is the gas constant, *T* is the temperature, φ is the potential, ε_0 and ε_r are the vacuum permittivity and medium dielectric constant, respectively.

At the carbon layer surface, the flux of the redox molecules *O* and *R* are determined by the Bulter-Volmer equations:

$$J_R = k^0 c_O e^{-\alpha f(V - V_{sol} - E^{0\prime})} - k^0 c_R e^{(1-\alpha) f(V - V_{sol} - E^{0\prime})} \quad \text{(r= a+z*tanθ,, H <z<0)} \qquad \text{(S3)}$$

$$J_O = -k^0 c_O e^{-\alpha f(V - V_{sol} - E^{0\prime})} + k^0 c_R e^{(1-\alpha) f(V - V_{sol} - E^{0\prime})} \quad \text{(r= a+z*tanθ,, H<z<0)} \qquad \text{(S4)}$$

V is the applied potential, k^0 and $E^{0\prime}$ are the standard rate constant and formal potential for the electron transfer process. *f* = F/RT, V_{sol} is solution potential, and α is the transfer coefficient. The total electronic current, i_T, was thus calculated by integrating the total flux of the *O* species at the carbon layer:

$$i_T = F \int J_O dS$$

Solutions

Dopamine hydrochloride and ascorbic acid were purchased from Sigma−Aldrich (St. Louis, MO). A 10 mM stock solution was prepared in $HClO_4$, and were diluted daily to the desired concentration in phosphate buffered saline (131.3 mM NaCl, 3.00 mM KCl, 10 mM NaH_2PO_4, 1.2 mM $MgCl_2$, 2.0 mM Na_2SO_4, and 1.2 mM $CaCl_2$ with the pH adjusted to 7.4).

For brain slice experiments, artificial cerebral spinal fluid (aCSF) was utilized in place of PBS. The aCSF (126 mM NaCl, 2.5 mM KCl, 1.2 mM NaH_2PO_4, 2.4 mM $CaCl_2$ dehydrate, 1.2 mM $MgCl_2$ hexahydrate, 25 mM $NaHCO_3$, 11 mM glucose, and 15 mM tris (hydroxymethyl) aminomethane) was made daily and adjusted to pH 7.4. 150 μM solutions of dopamine were made in room temperature aCSF each day of biological experimentation.