Supporting Information for:

Nanopipet-based Liquid-Liquid Interface Probes for the Electrochemical Detection of Acetylcholine, Tryptamine, and Serotonin via Ionic Transfer

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Table S1. Parameters for pulling nm orifice pipets.

Figure S1. Cyclic voltammogram of 1 mM acetylcholine and SEM image of pipet to show diffusion coefficient determination.

Figure S2. Cyclic voltammogram of 1 mM tryptamine and SEM image of pipet to show diffusion coefficient determination.

Figure S3. Cyclic voltammogram of 1 mM serotonin and SEM image of pipet to show diffusion coefficient determination.

Figure S4. Cyclic voltammogram of serotonin in artificial sea water.

Figure S5. Cyclic voltammograms of dopamine, ascorbic acid, γ-aminobutric acid in artificial sea water. With Cyclic voltammogram of TEA shown as reference.

Figure S6. Cyclic voltammograms of dopamine, ascorbic acid, γ-aminobutric acid in LiCl. With Cyclic voltammogram of TEA shown as reference.

Figure S7. Calibration curve for cyclic voltammetry of acetylcholine.

Figure S8. Calibration curve for cyclic voltammetry of tryptamine.

Figure S9. Calibration curve for amperometry of acetylcholine.

Figure S10. Calibration curve for amperometry of tryptamine.

Figure S11. Calibration curve for cyclic voltammetry of serotonin.

Figure S12. Calibration curve for amperometry of serotonin.

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Table S1. Pulling parameters for nm orifice pipets using a P-2000 Laser-Based Micropipette Puller (Sutter Instrument, Novato, CA) with quartz glass capillaries (O.D. = 1.0 mm; I.D. = 0.70 mm; 10 cm length).

Heat	Fil	Vel	Del	Pul
725	4	55	130	100

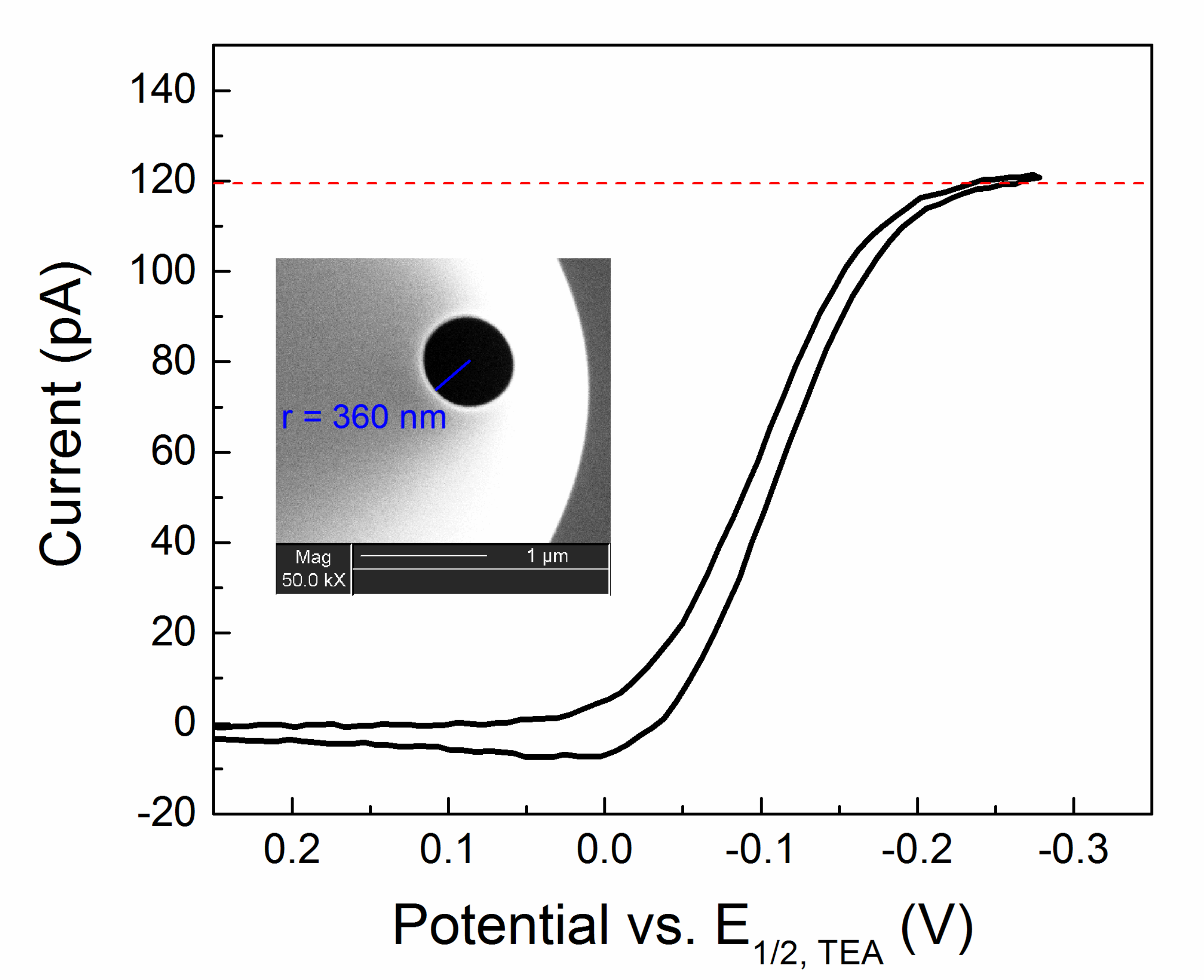

Figure S1. SEM and cyclic voltammogram for one of the pipets used for calculating the diffusion coefficient of acetylcholine (ACh) in artificial sea water (ASW) via Cell 1. Concentration of ACh = 1 mM; steady state current = 120 pA (red dashed line). Inset: SEM image of pipet used, showing a radius of 360 nm. Calculated D_{Ach} = 7.02 x 10^{-6} cm^2/s.

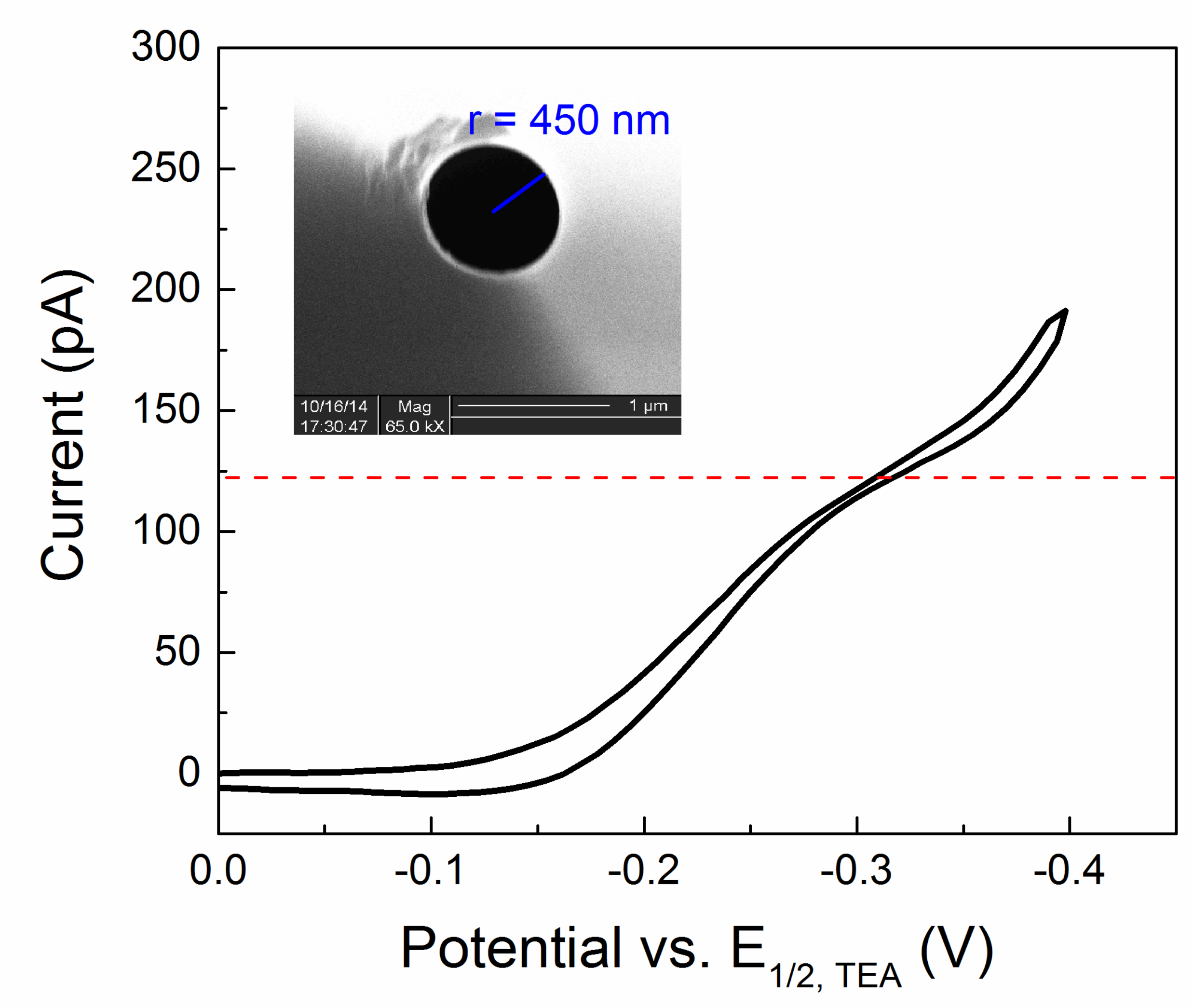

Figure S2. SEM and cyclic voltammogram for one of the pipets used for calculating the diffusion coefficient of tryptamine (T) in artificial sea water (ASW) via Cell 1. Concentration of T = 1 mM; Steady state current = 126 pA (red dashed line); the process shown at more negative potentials is due to the transfer of ASW. Inset: SEM image of pipet used, showing a radius of 450 nm. Calculated $D_T = 5.90 \times 10^{-6}$ cm^2/s.

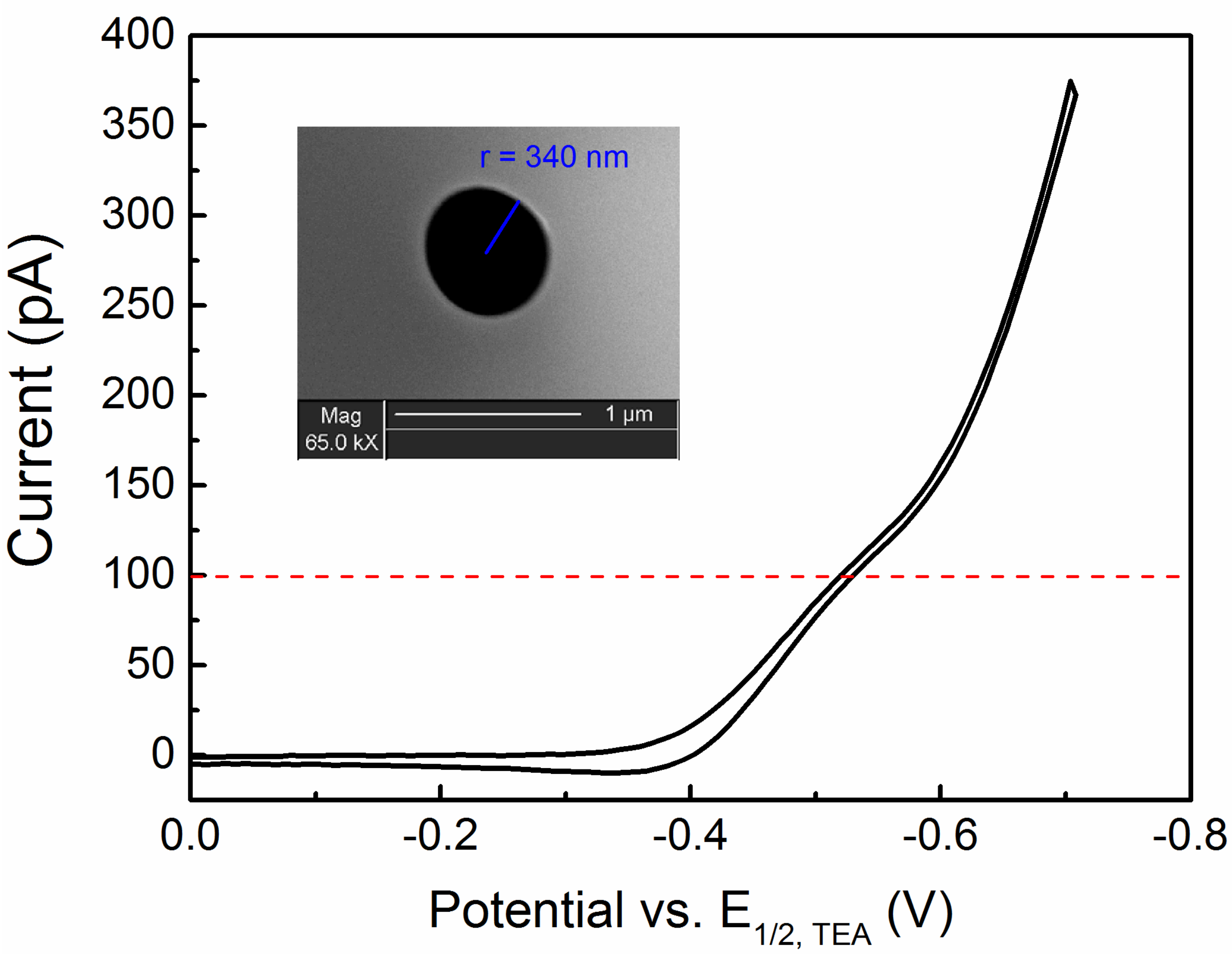

Figure S3. SEM and cyclic voltammogram for one of the pipets used for calculating the diffusion coefficient of serotonin (5-HT) in 10 mM LiCl via Cell 2. Concentration of 5-HT = 1 mM; Steady state current = 100 pA (red dashed line); the process shown at more negative potentials is due to the transfer of LiCl. Inset: SEM image of pipet used, showing a radius of 340 nm. Calculated $D_{5\text{-HT}} = 6.20 \times 10^{-6}$ cm^2/s.

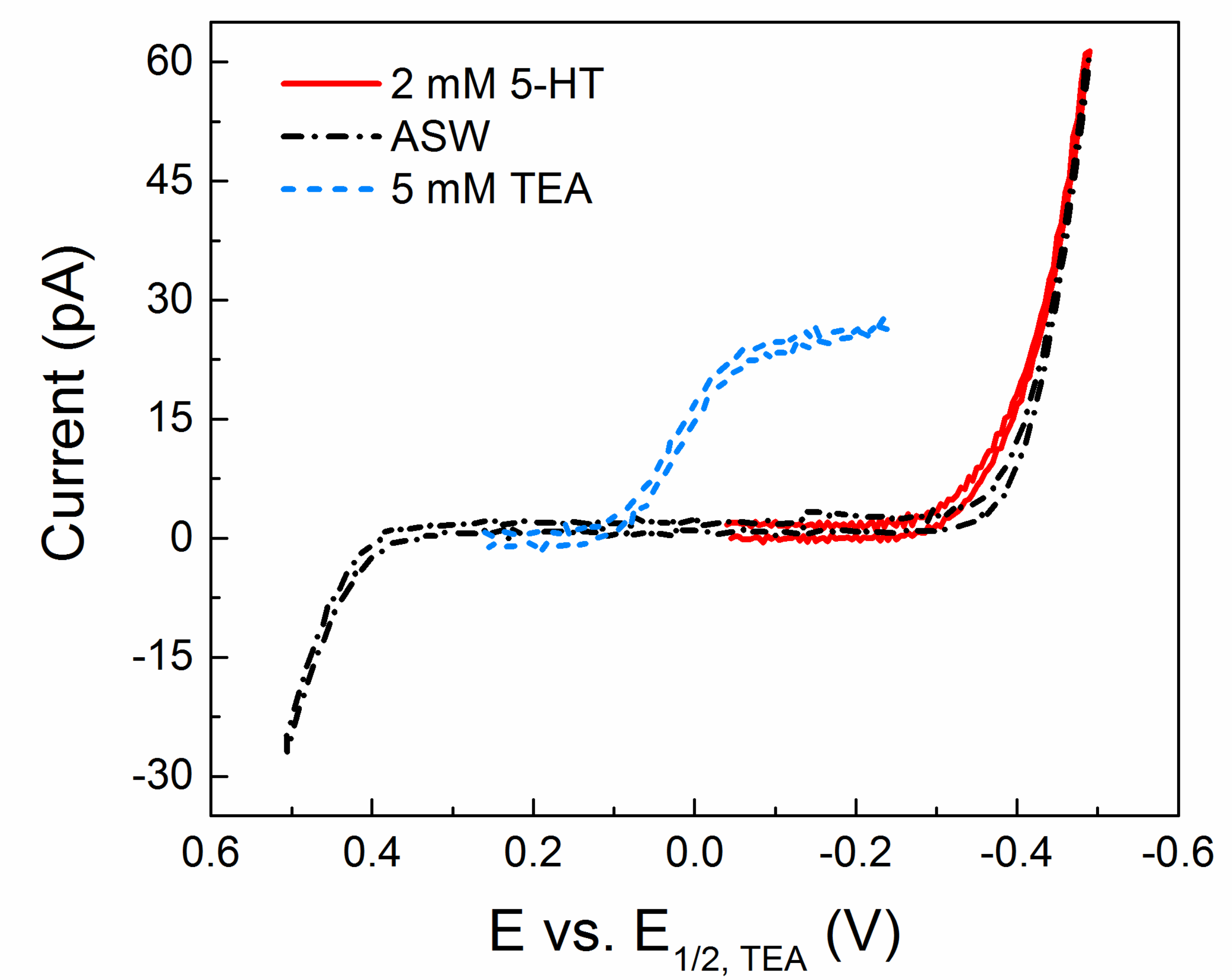

Figure S4. Cyclic voltammogram of 2 mM serotonin (5-HT) in artificial sea water (ASW) using a pipet with a radius of 28 nm in Cell 3. Blue dashed line represents 5 mM TEA.

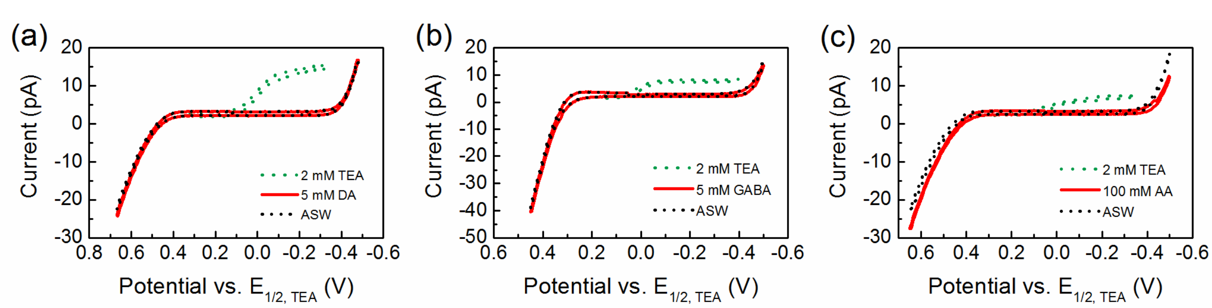

Figure S5. Cyclic voltammograms of (a) 5 mM dopamine (DA), (b) 100 mM ascorbic acid (AA), and (c) 5 mM γ-aminobutric acid (GABA) in artificial sea water (ASW). Tetraethylammonium (TEA) was added at the end of each experiment to show that the probes used were working properly, ensuring that lack of signal from the possible intereferents is because they do not transfer within the potential window of ASW.

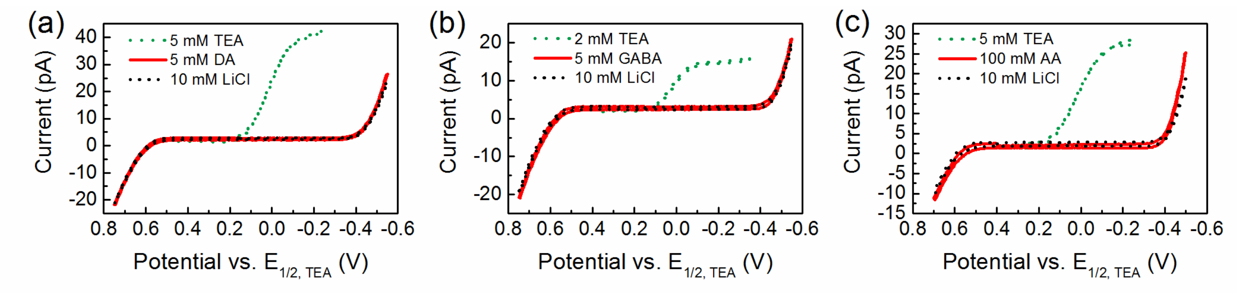

Figure S6. Cyclic voltammograms of (a) 5 mM dopamine (DA), (b) 100 mM ascorbic acid (AA), and (c) 5 mM γ-aminobutric acid (GABA) in 10 mM LiCl. Tetraethylammonium (TEA) was added at the end of each experiment to show that the probes used were working properly, ensuring that lack of signal from the possible intereferents is because they do not transfer within the potential window of LiCl.

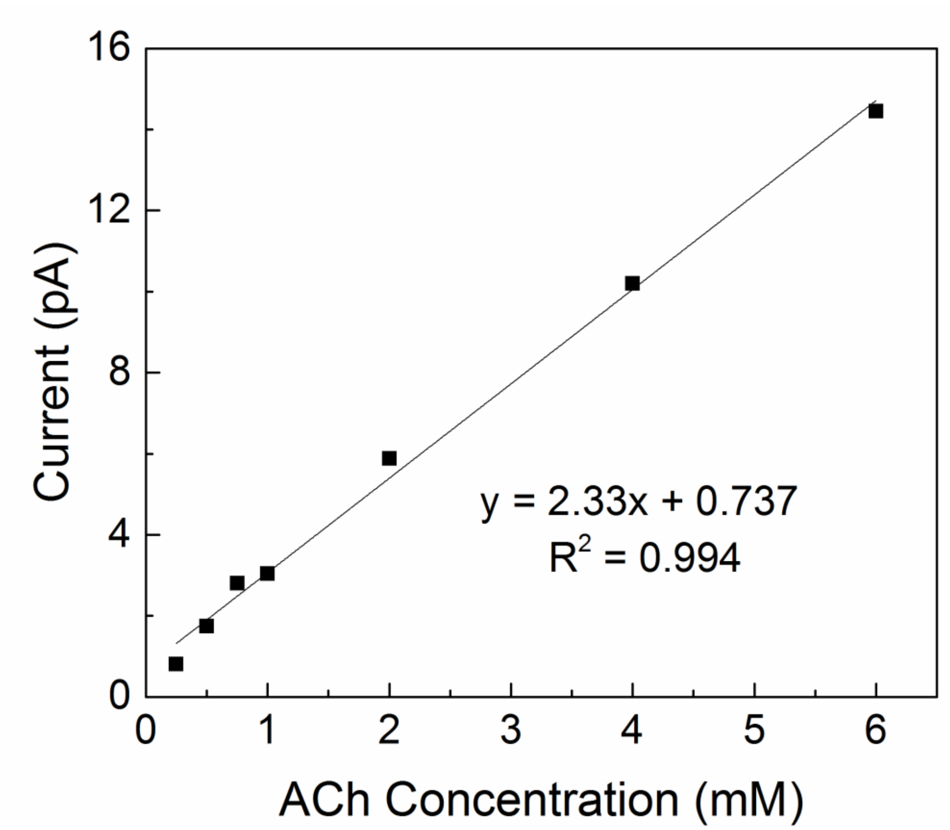

Figure S7. Background subtracted calibration curve for cyclic voltammograms of 0.25 – 6 mM acetylcholine (ACh) using a pipet with a radius of 7 nm in Cell 1. Current was read at -0.25 V vs. $E_{1/2,\ TEA}$ in Figure 3a.

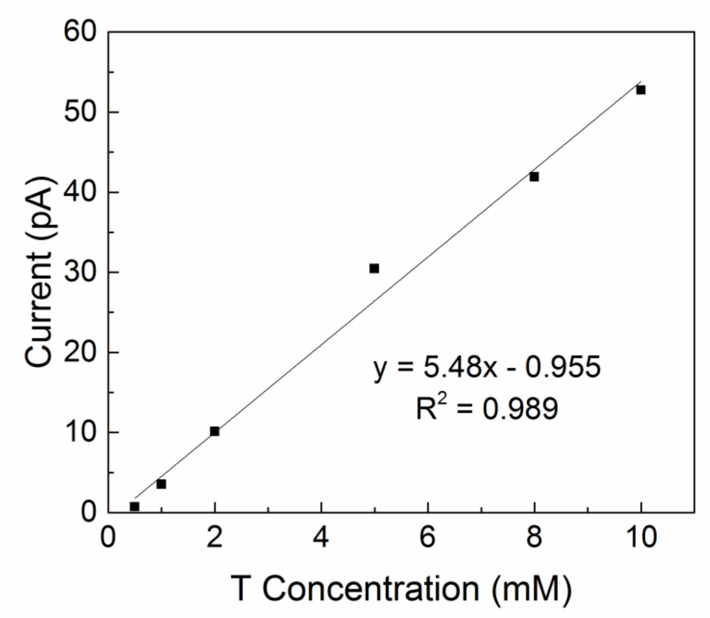

Figure S8. Background subtracted calibration curve for cyclic voltammograms of 0.5 – 10 mM tryptamine (T) using a pipet with a radius of 19 nm in Cell 1. Current was read at -0.32 V vs. $E_{1/2,\ TEA}$ in Figure 3c.

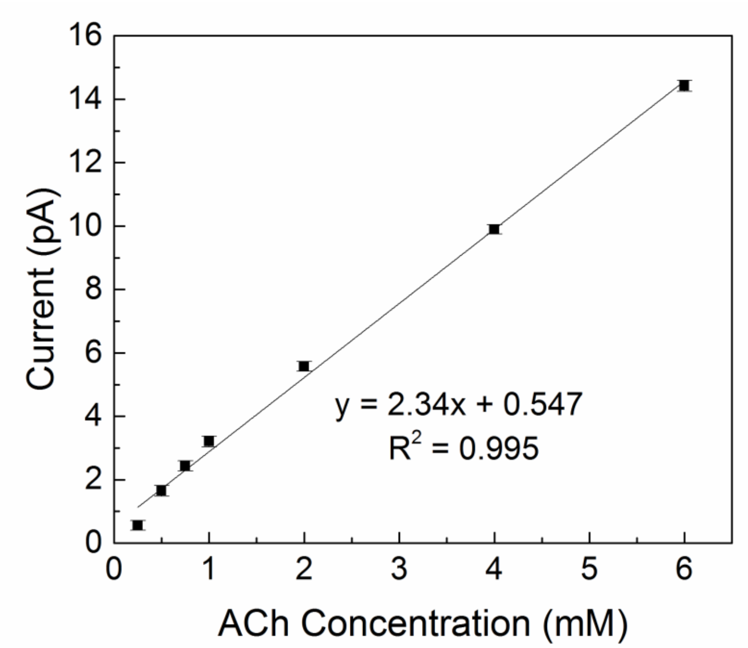

Figure S9. Background subtracted calibration curve for amperometry of acetylcholine (ACh) based on Figure 3b. Applied potential = -0.25 V vs. $E_{1/2,\ TEA}$. Data points represent the average current over 50.0 s, and error bars represent standard deviation. Measurements were made using Cell 1.

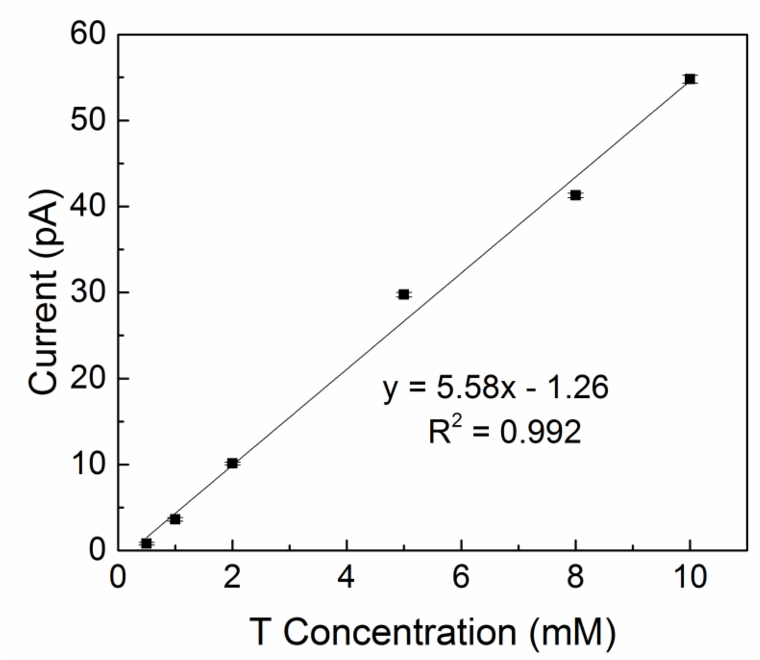

Figure S10. Background subtracted calibration curve for amperometry of tryptamine (T) based on Figure 3d. Applied potential = -0.32 V vs. $E_{1/2,\ TEA}$. Data points represent the average current over 50.0 s, and error bars represent standard deviation. Measurements were made using Cell 1.

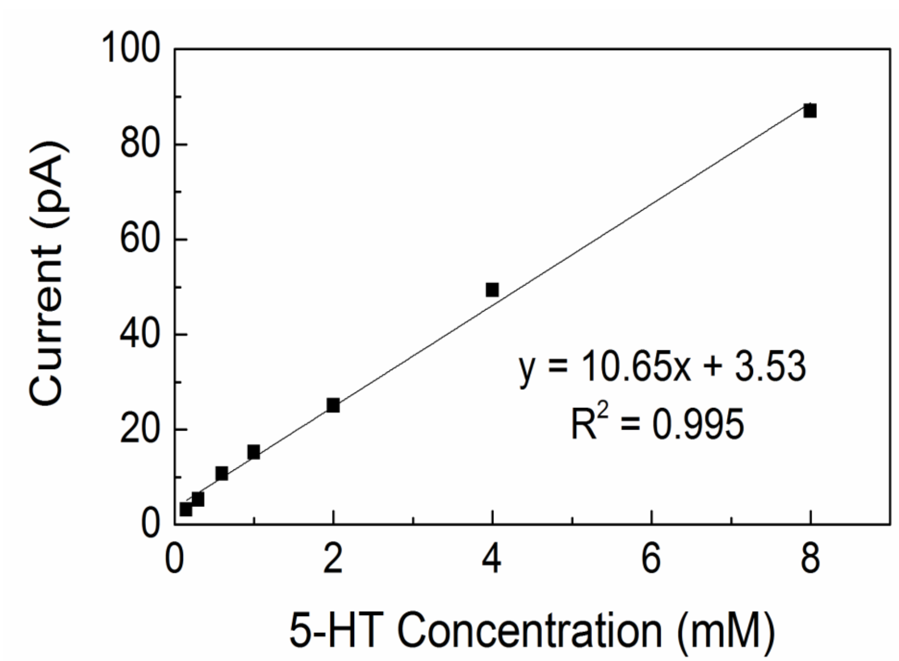

Figure S11. Background subtracted calibration curve for cyclic voltammograms of 0.15 – 8 mM serotonin (5-HT) using a pipet with a radius of 35 nm in Cell 2. Current was read at -0.51 V vs. $E_{1/2,\ TEA.}$

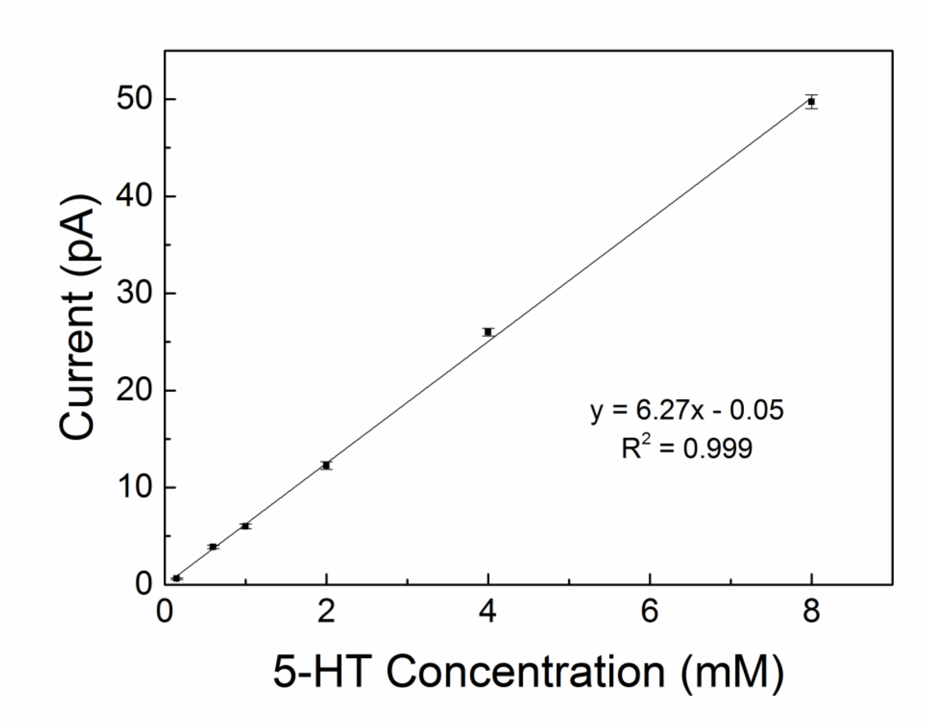

Figure S12. Background subtracted calibration curve for amperometry of serotonin (5-HT) based on Figure 4b. Applied potential = -0.52 V vs. $E_{1/2,\ TEA}$. Data points represent the average current over 50.0 s, and error bars represent standard deviation. Measurements were made using a pipet with a radius of 21 nm using Cell 2.