

Supporting Information

Highly sensitive and selective detection of dopamine using overoxidized polypyrrole/sodium dodecyl sulfate-modified carbon nanotube electrodes

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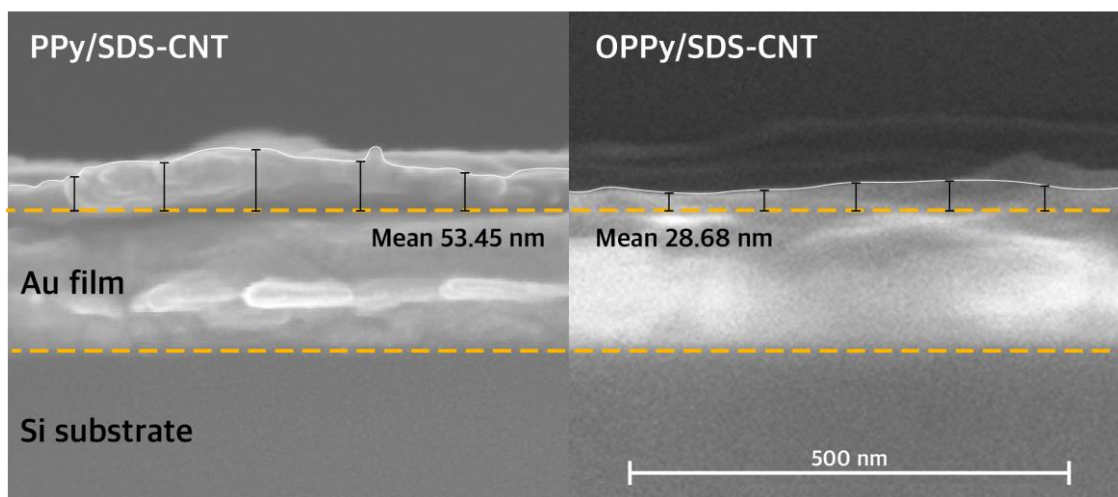


Figure S1. Cross-sectional SEM images of PPy/SDS-CNT electrode and OPPy/SDS-CNT electrode (PPy/SDS-CNT: SU8200, Hitachi, Japan; OPPy/SDS-CNT: Magellan400, FEI, USA). The thickness was obtained by averaging the value of five sampling points.

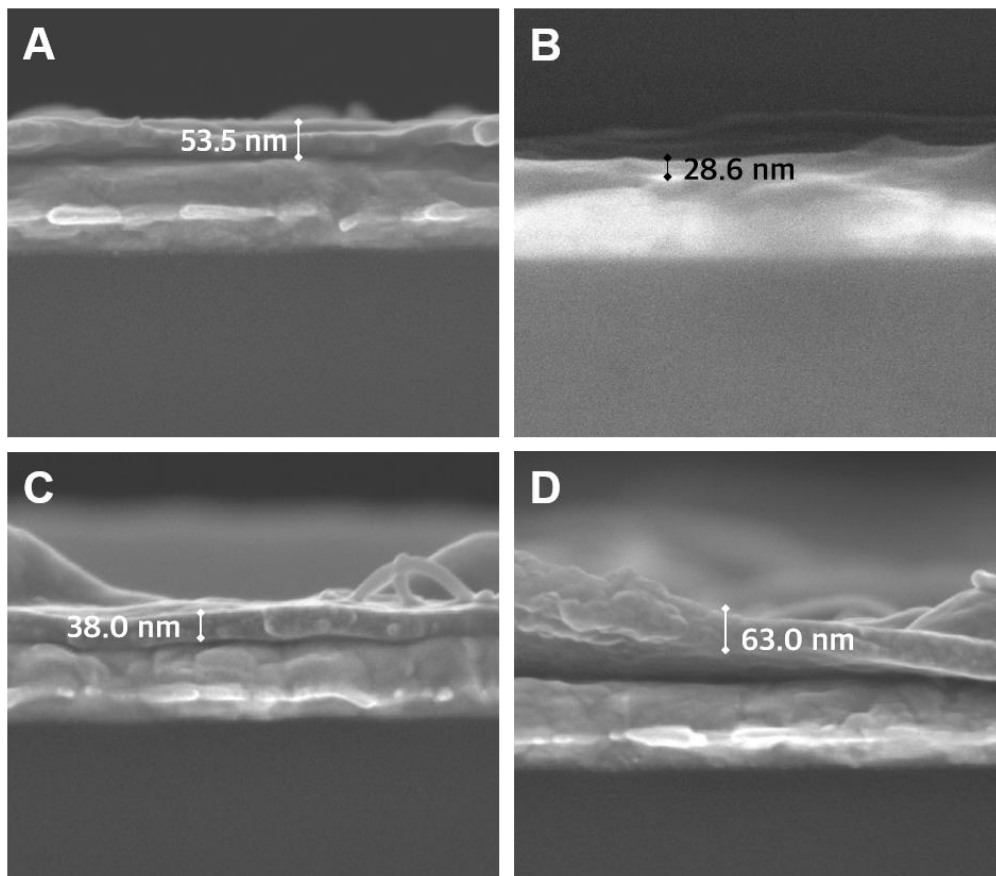


Figure S2. Cross-sectional SEM images of (A) PPy/SDS-CNT electrode with 5 s deposition time, (B) OPPy/SDS-CNT electrode with 10 s, (C) OPPy/SDS-CNT electrode with 20 s, and (D) OPPy/SDS-CNT electrode with 40 s. A, C, and D were obtained using SU8200, Hitachi, Japan while B was measured using Magellan400, FEI, USA.

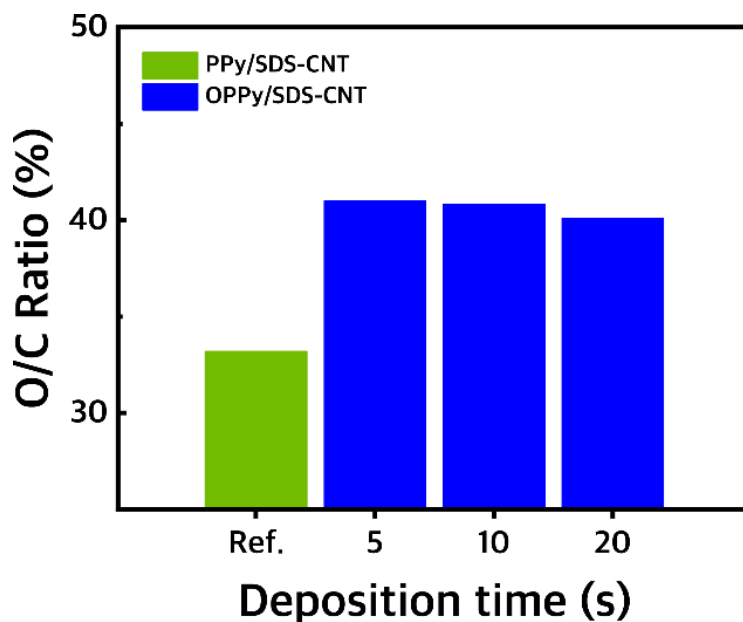


Figure S3. Atomic ratio of oxygen and carbon (O/C ratio) as a function of deposition time (film thickness). The data was measured by the top-view energy dispersive spectrometer (EDS). O/C ratio of the PPy/SDS-CNT electrode is shown as a comparison.

Method: To identify the penetration depth of overoxidation, we measured energy dispersive spectroscopy (EDS) for different thicknesses of OPPy/SDS-CNT composite films. Three samples of OPPy/SDS-CNT electrodes were fabricated with different deposition time (5 s, 10 s, and 20 s) and were overoxidized under the same condition. Atomic percent ratio of oxygen and carbon was analyzed with top-view EDS. The EDS measured atomic content for the volume of 1 μm depth from the surface, and all of the film thickness was under 1 μm . If the oxidation reaction was only for the surface, the atomic percent of carbon would have increased as the thickness of the film increased. The average oxygen/carbon ratio was $\sim 40.6\%$ with a standard deviation of 0.387%. The data did not show any special tendency to the thickness. This indirectly indicates that the oxidation reaction also occurred inside the material, at least for the thickness range we have considered.

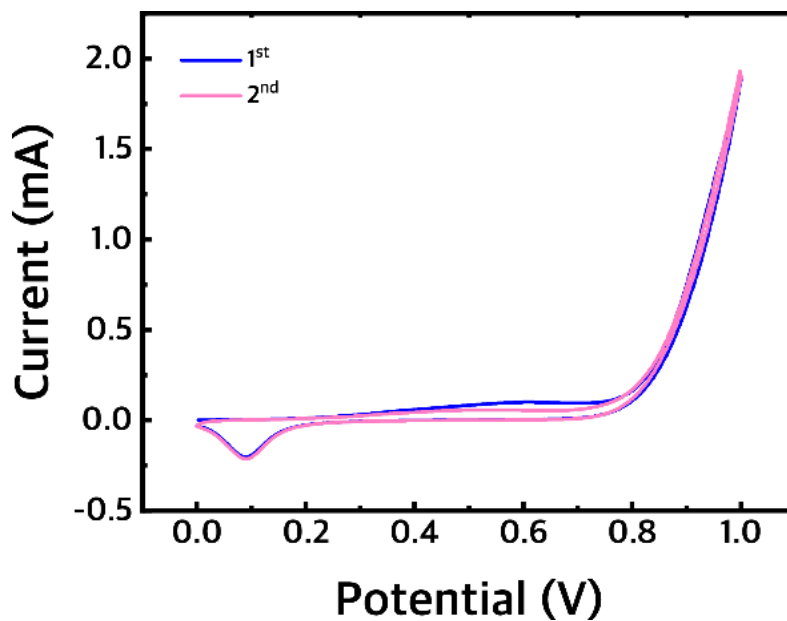


Figure S4. Cyclic voltammogram of CNT/Au electrode during the NaOH treatment process in 0.1 M NaOH solution. The potential was swept from 0 to 1 V twice with a scan rate of 50 mV/s.

Method: The chemical change of CNT during the overoxidation process was investigated. We fabricated five NaOH-treated CNT Au electrodes and five untreated CNT/Au electrodes and compared the sensing performance. The data were averaged for each electrode group. 25 mg of pristine CNT was dispersed in 50 ml of deionized water by sonicating for 40 min. After the sonication, CNT was drop cast onto an Au electrode. We measured cyclic voltammetry of the CNT/Au electrodes at the 0.1 M NaOH solution under the same condition as our pyrrole overoxidation step.

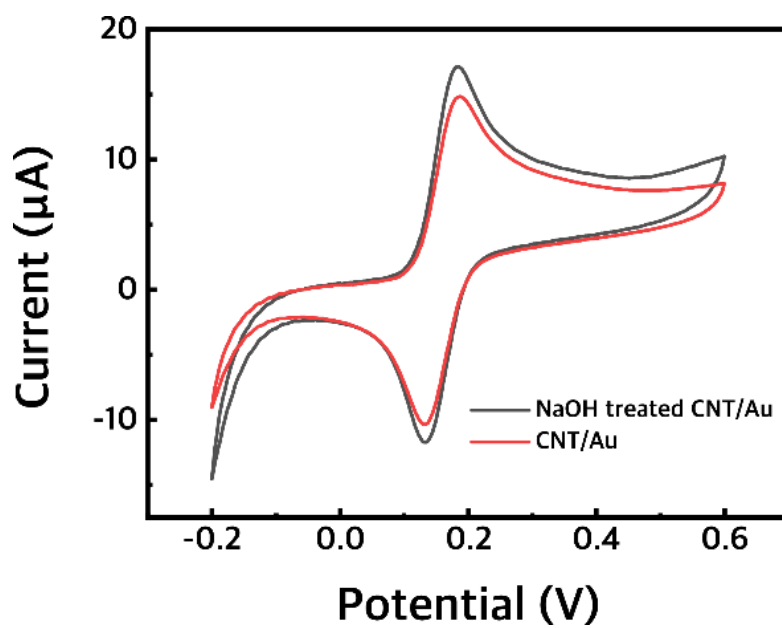


Figure S5. Cyclic voltammetry of NaOH-treated CNT/Au electrode and non-treated CNT/Au electrode in PBS buffer (pH 7.4) containing 100 μM DA ($n=5$). The potential was swept from -0.2 V to 0.6 V with a scan rate of 50 mV/s.

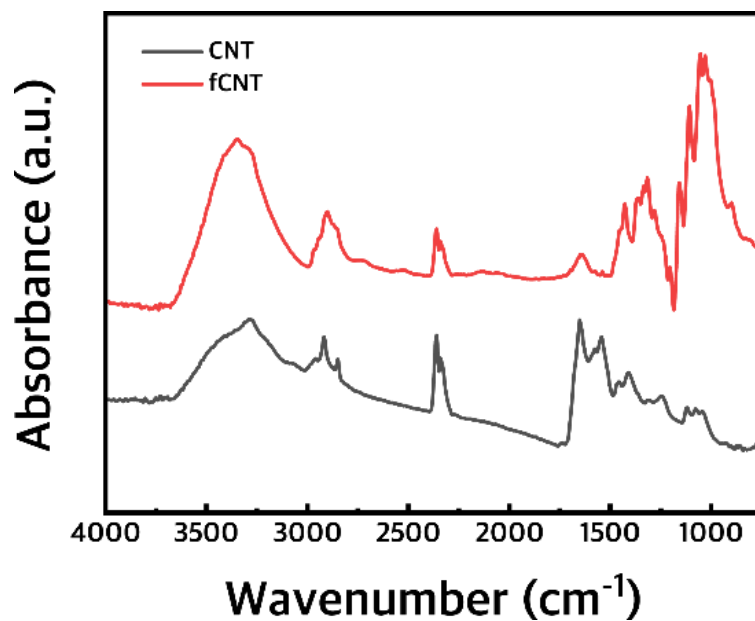


Figure S6. FTIR spectra of pristine CNT and fCNT (Nicolet™ iN10 MX Infrared Imaging Microscope, Thermo Scientific™, USA). Pristine CNT was functionalized by refluxing with 70% w/w HNO₃ for 1.5 h at 140°C. After the refluxing step, CNT was separated from the mixture using a centrifuge (10000 rpm, 25°C, 10 min) and dilution step. The separation step was repeated for 5 times. After the functionalization, peaks in the range of 100-1200 cm⁻¹ was observed. This result implies the carboxyl group is successfully attached to the surface of the CNT.

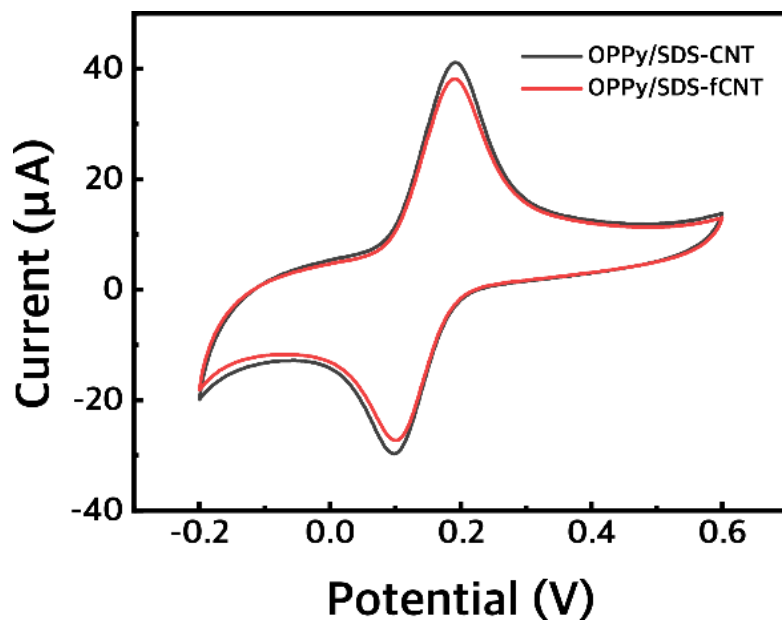


Figure S7. Cyclic voltammogram of OPPy/SDS-CNT electrode and OPPy/SDS-fCNT electrode in PBS buffer (pH 7.4) containing 100 μM DA (n=3). The potential was swept from -0.2 V to 0.6 V with a scan rate of 50 mV/s.

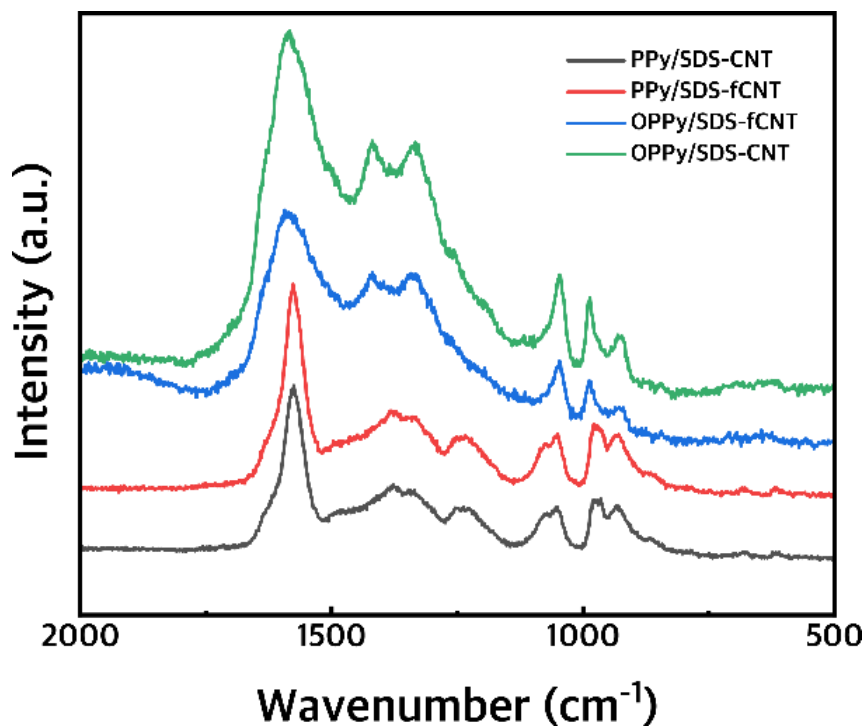


Figure S8. Raman spectra of PPy/SDS-CNT, PPy/SDS-fCNT, OPPy/SDS-CNT and OPPy/SDS-fCNT electrode at the wavelength of 514 nm (LabRAM HR Evolution Visible_NIR, HORIBA France SAS).

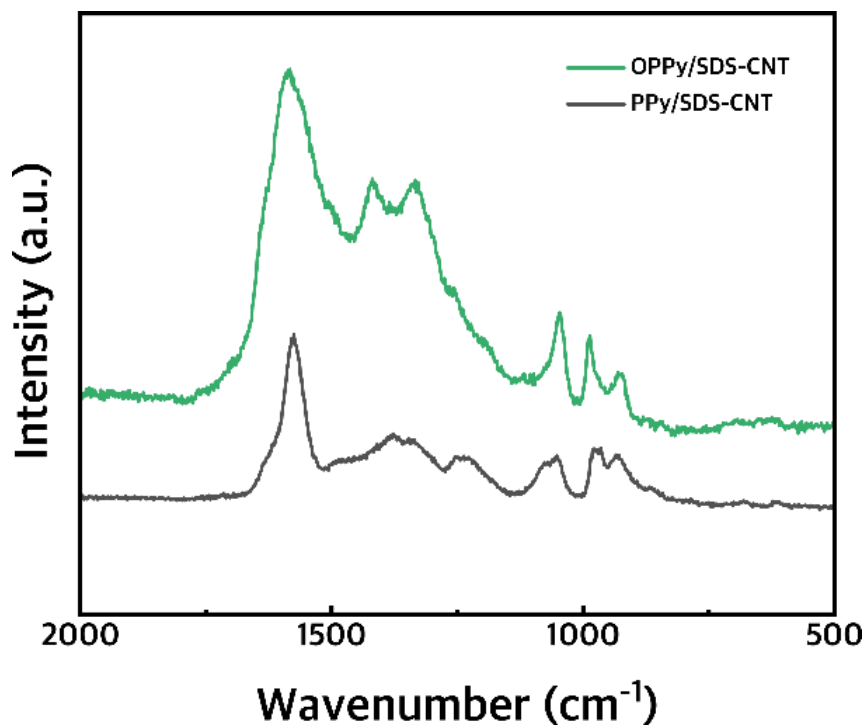


Figure S9. Raman spectra of PPy/SDS-CNT and OPPy/SDS-CNT electrode at the wavelength of 514 nm.

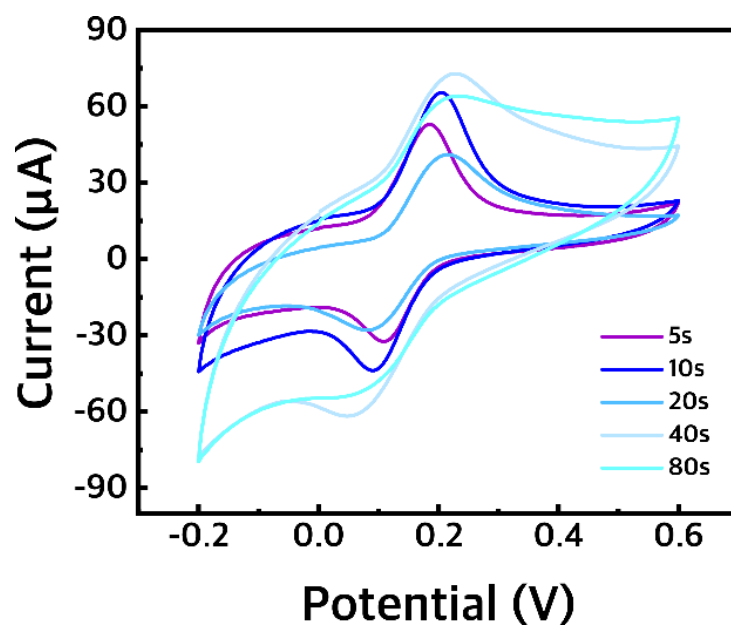


Figure S10. Cyclic voltammogram of OPPy/SDS-CNT electrodes fabricated with varying deposition time (5 s, 10 s, 20 s, 40 s, and 80 s) in PBS buffer (pH 7.4) containing 100 μM DA. The potential was swept from -0.2 V to 0.6 V with a scan rate of 50 mV/s.

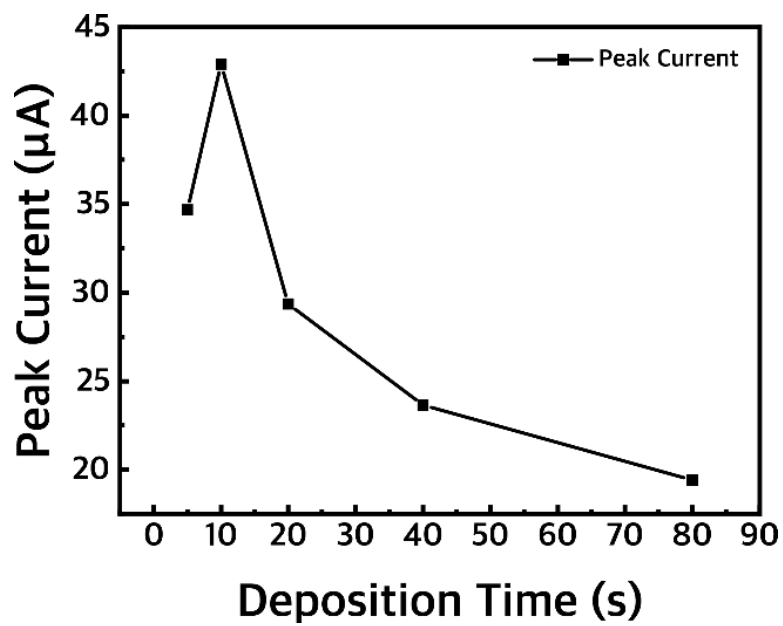


Figure S11. Plot of peak currents of CV in PBS buffer (pH 7.4) containing 100 μM DA as a function of the deposition time of PPY/SDS-CNT films.

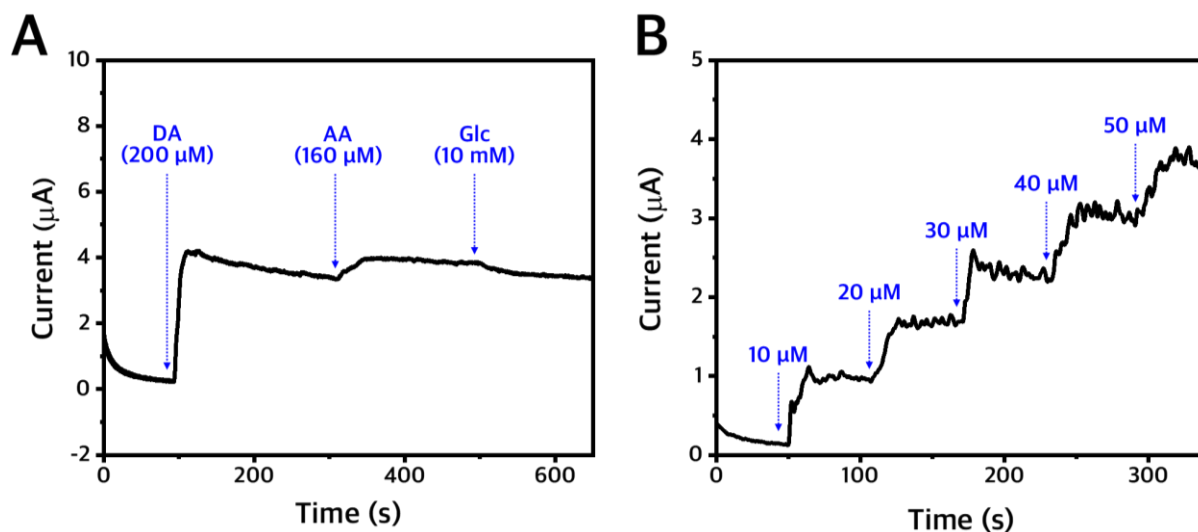


Figure S12. (A) Transient amperometric current in response to DA, AA and Glu injection measured using the OPPY/SDS-CNT electrode. (B) Transient amperometric current in response to various concentrations of DA measured using the OPPY/SDS-CNT electrode. A constant voltage of 1.8 V was applied on the electrode for all measurements.

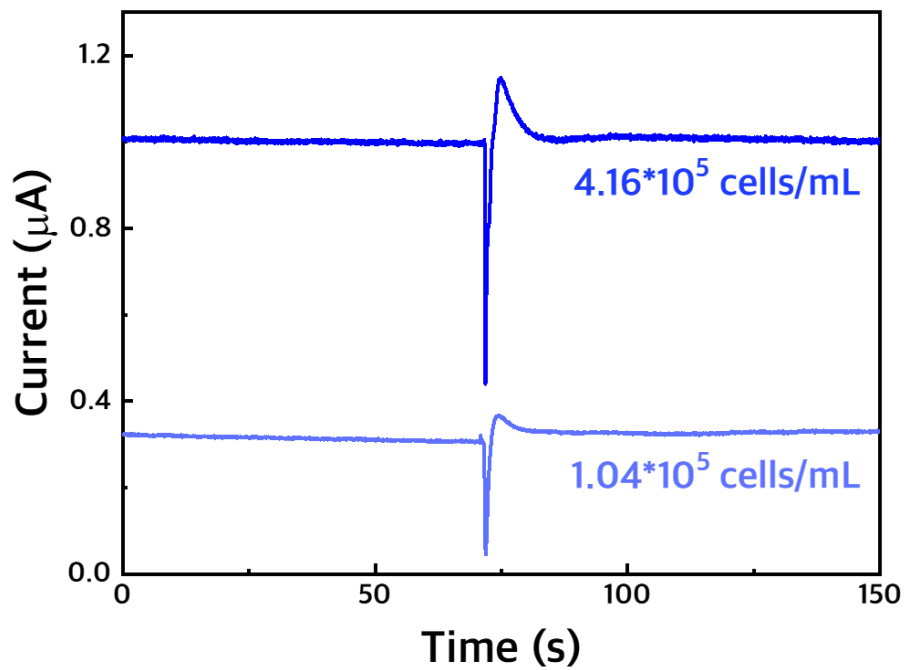


Figure S13. Transient amperometric currents measured using the OPPy/SDS-CNT electrode from two different concentrations of PC12 cells (1.04×10^5 and 4.16×10^5 cells/mL).

Table S1. Peak current statistics from the cyclic voltammogram of NaOH treated CNT/Au electrode and non-treated CNT/Au electrode. Sample #1 and sample #10 was regarded as outliers. * I_{pa} : anodic peak current.

NaOH-treated Sample #	I_{pa} (μ A)	Baseline (μ A)	Peak (μ A)	Mean (μ A)	S.D. (μ A)
1	14.7	1.5	13.2		
3	17.7	1.5	16.2		
5	17.4	1.5	15.9	16.2	0.5
7	18.5	1.5	17.0		
9	17.4	1.5	15.8		
Non-treated Sample #	I_{pa} (μ A)	Baseline (μ A)	Peak (μ A)	Mean (μ A)	S.D. (μ A)
2	14.7	1.2	13.5		
4	14.6	1.2	13.4		
6	14.7	1.2	13.4	13.4	0.2
8	14.3	1.2	13.1		
10	15.9	1.2	14.6		

Table S2. Peak current statistics from the cyclic voltammogram of OPPy/SDS-CNT electrode and OPPy/SDS-fCNT electrode. * I_{pa} : anodic peak current.

OPPy/SDS-CNT Sample #	I_{pa} (μ A)	Baseline (μ A)	Peak (μ A)	Mean (μ A)	S.D. (μ A)
1	40.7	12.0	28.6		
2	41.5	10.7	30.8	30.5	1.45
3	41.4	9.24	32.2		
OPPy/SDS-fCNT Sample #	I_{pa} (μ A)	Baseline (μ A)	Peak (μ A)	Mean (μ A)	S.D. (μ A)
1	40.1	10.5	29.6		
2	30.9	10.9	20.0	26.4	4.56
3	35.8	6.10	29.7		

Table S3. Peak area, total number of electrons, total number of oxidized DA molecules, and mole of oxidized DA molecules calculated from different concentrations of PC12 cells in Figure S13.

The oxidation peak in Figure S13 was integrated through peak integration analysis provided by Origin. The peak area corresponded to the total charge generated when DA molecules were oxidized. Considering that 2 electrons were emitted by the electrochemical oxidation of single DA molecule, the number of oxidized molecules can be calculated by dividing the total charges with the charges of 2 electrons. Finally, mole was calculated by dividing the number of molecules with Avogadro's number.

	4.16 × 10⁵ cells/mL	1.04 × 10⁵ cells/mL
Peak area from Figure S13	6.26 × 10 ⁻⁷ C	3.28 × 10 ⁻⁷ C
Total number of electrons = (total charge)/(elementary charge)	3.91 × 10 ¹²	2.05 × 10 ¹²
Total number of oxidized DA molecules = (total number of electrons)/2	1.95 × 10 ¹²	1.03 × 10 ¹²
Mole of oxidized DA molecules = (total number of oxidized DA molecules) /(Avogadro's number)	3.24 × 10 ⁻¹² mole	1.7 × 10 ⁻¹² mole

(Elementary charge = 1.6021773349*10⁻¹⁹ C; Avogadro's number = 6.0221409*10²³ mol⁻¹)