***Supporting Information for*:**

Electrodeposited Gold on Carbon-Fiber Microelectrodes for Enhancing Amperometric Detection of Dopamine Release from Pheochromocytoma Cells

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Experimental Section

Additional Discussion of Table 2. The number of cells measured for each probe sub-type are as follows: Bare CFE = 18 cells, -0.3 V = 13 cells, -0.4 V = 16 cells, -0.5 V = 9 cells, -0.6 V = 13 cells.

Electrodeposition of Platinum. Pt was electrodeposited from 1 mM $PtCl_4^-$, 0.5 mM H_2SO_4 onto beveled CFEs using a pulsed electrodeposition procedure. $E_{deposit}$ = -1.6 V was applied for 0.2 s, then E_{rest} = 0 V was applied for 0.8 s to allow new metal ions to diffuse to the surface of the CFE. This was repeated for 75 cycles. Quartile potentials $E_{1/4}$, $E_{1/2,}$ $E_{3/4}$, were extracted from dopamine CVs using a custom-written algorithm. Electrochemical surface area (ECSA) and surface roughness factor, ρ, were extracted from CV scans in 0.5 M H_2SO_4 by finding the area under the gold oxide reduction wave.

Ca^{2+}-free Experiment. Ca^{2+}-free media was prepared to test whether Au-CFEs detected intracellular vesicles via VIEC. Ca^{2+}-free saline was: 150 mM NaCl, 5 mM KCl, 1.2 mM $MgCl_2 \cdot 6H_2O$, 5 mM glucose, 10 mM HEPES, and 0.5 mM EGTA (ethylene glycol-bis(β-aminoethyl ether)-N,N,N',N'-tetraacetic acid). Electrodes were lowered gently onto cells and perfused with a Ca^{2+}-free stimulation solution to mimic the normal experiment. Cells were measured for 30 seconds in this manner before moving onto the next cell. 3 probes of each subtype were used to measure 10-12 cells. No events were observed in the absence of Ca^{2+}.

Table S1. $E_{1/2}$ values for oxidation of dopamine on the CFEs before and after gold deposition.

$E_{deposit}$ (V)	# Electrodes	$E_{1/2}$ before Au (mV)	$E_{1/2}$ after Au (mV)
-0.3	13	155±9.6	84.7±12.5
-0.4	14	159±15.8	90.1±11.3
-0.5	10	174±19.8	66.1±14.2
-0.6	10	157±19.9	81.9±19.9

Table S2. Spike Characteristics collected using Pt-CFEs on PC12 cells. * is p<0.05, ** is p<0.01.

Electrode	Cells	# events	I_{max} (pA)	$t_{1/2}$ (ms)	t_{rise} (ms)	t_{fall} (ms)	$N_{molecules}/10^3$
CFE	7	869	16.7±2.7	1.03±0.1	0.78±0.08	1.81±0.21	95.9±12.9
Pt-CFE	7	599	18.7±3.0	0.83±0.08*	0.69±0.06	1.26±0.18**	76.1±9

Table S3. Spike Characteristics collected from L-DOPA incubated PC12 cells. * is p<0.01, ** is p<0.0001.

Electrode	# Cells	Events	I_{max} (pA)	$t_{1/2}$ (ms)	t_{rise} (ms)	t_{fall} (ms)	$N_{molecules}/10^3$
Bare CFE	17	1768	11.7±1.1	1.79±0.11	1.30±0.07	3.04±0.27	135±10.2
Au (-0.4V)	13	1438	32.1±2.0**	1.69±0.21	1.36±0.16	2.73±0.43	199±19.2*

Figure S1. Zoomed in SEM image of the Au-CFE from Main-text, Figure 1B.

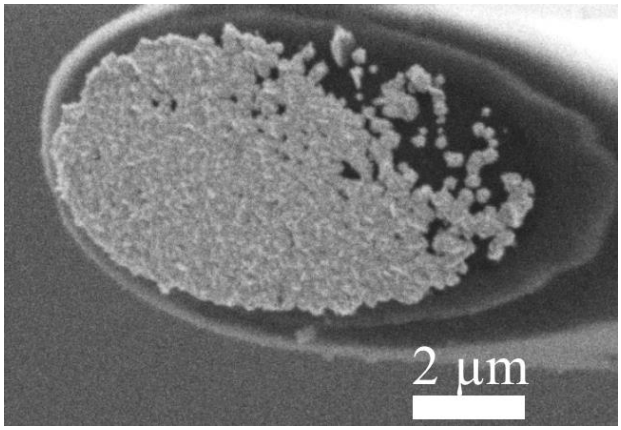

Figure S2. CVs in 0.1 mM dopamine, 1x PBS before (black) and after (gold) Au deposition. A) $E_{deposit}$ = -0.3 V, B) -0.4 V, C) -0.5 V, D) -0.6 V.

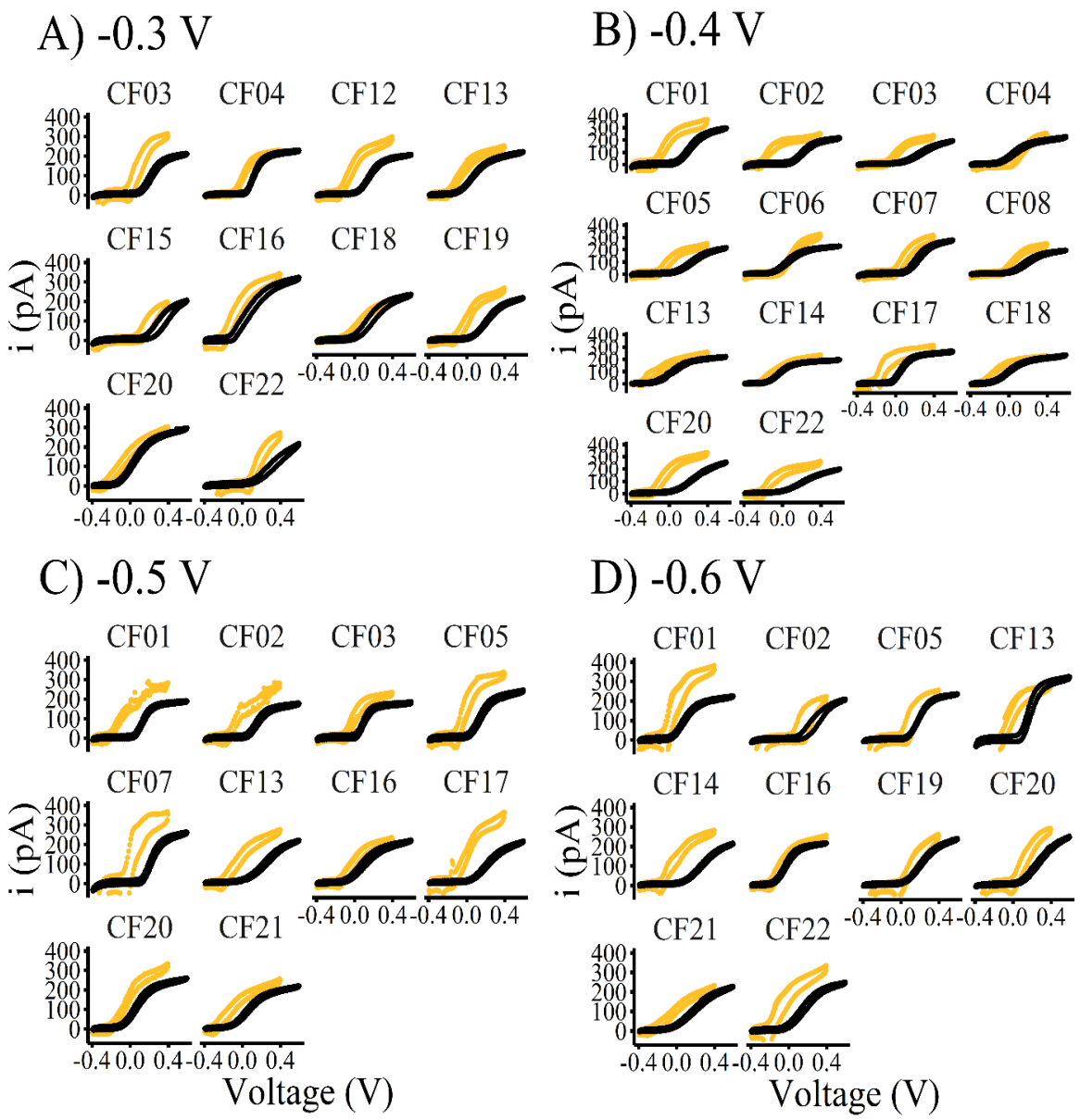

Figure S3. CVs in 0.5 M H_2SO_4 after Au deposition. A) $E_{deposit}$ = -0.3 V, B) -0.4 V, C) -0.5 V, D) -0.6 V.

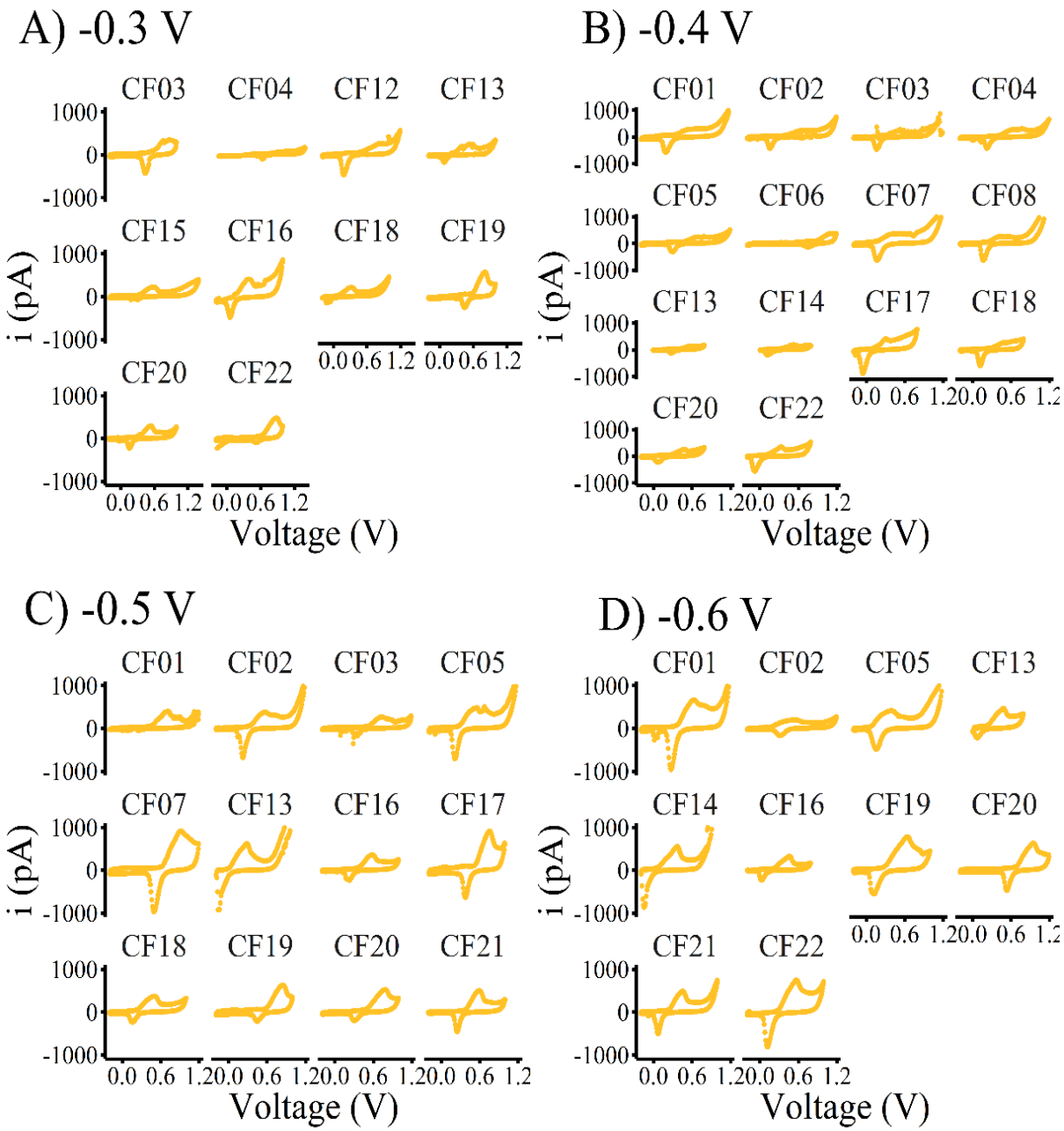

Figure S4. Additional amperometric traces at different $E_{deposit}$ conditions. A) Unmodified, bare CFEs, B) -0.3 V, C) -0.4 V, D) -0.5 V, and E) -0.6 V.

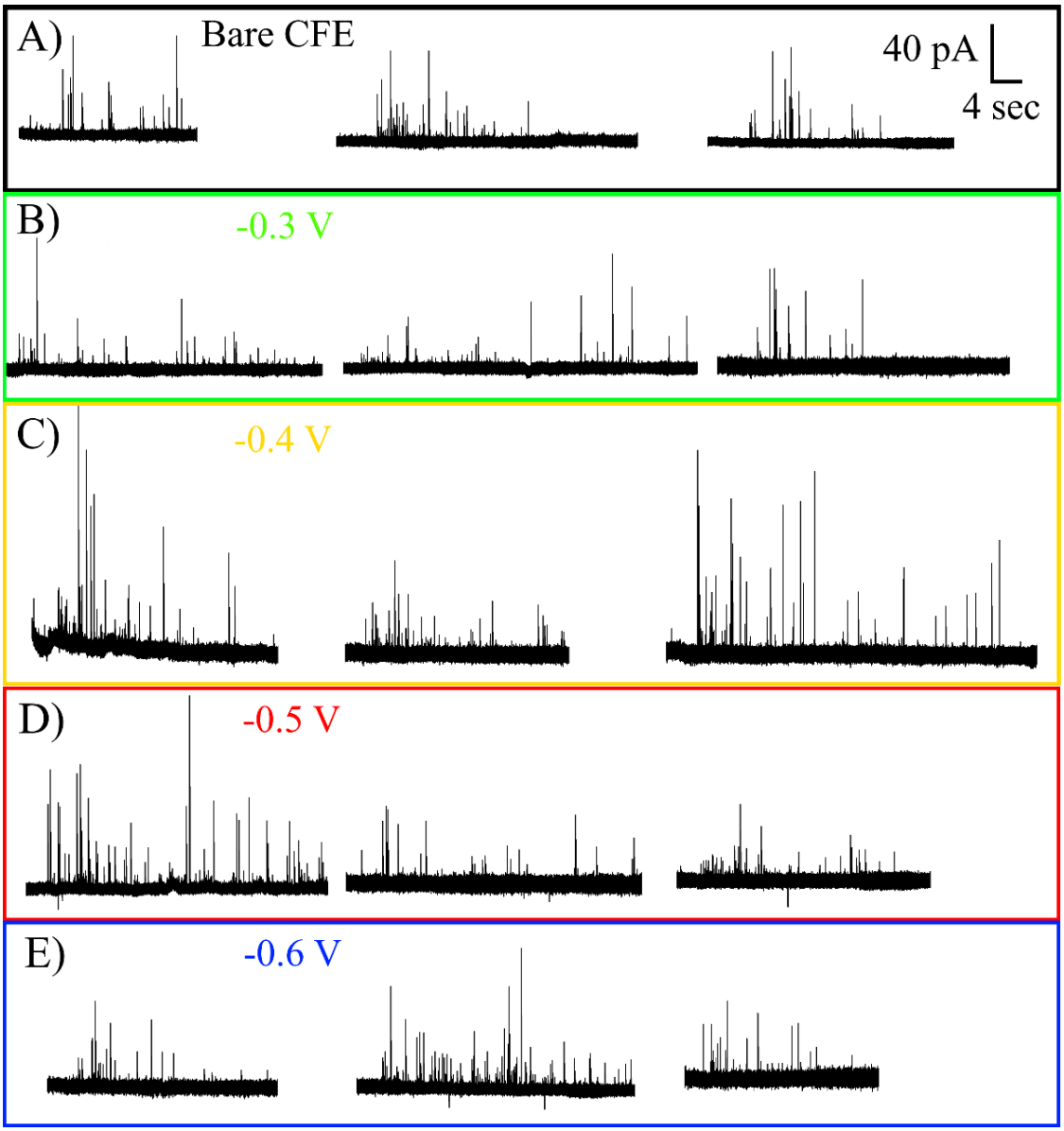

Figure S5. Example amperometric traces for Pt-CFEs on PC12 cells.

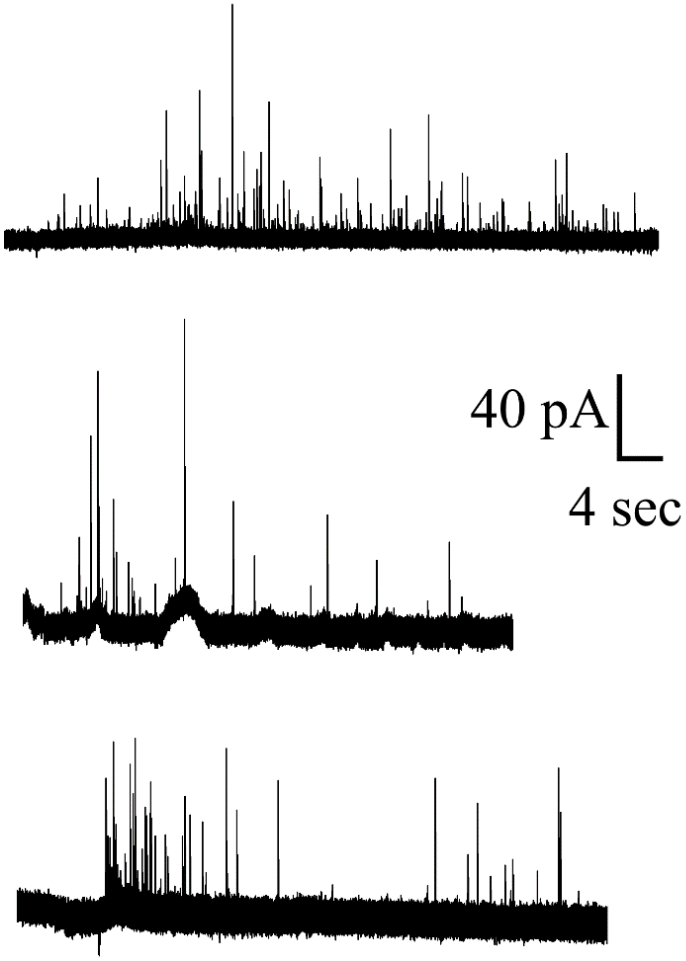

Figure S6. Pt-CFEs do not observe the same increased catecholamine release. A) Cumulative distributions of number of molecules released show no difference (KS-test, $p>0.05$) in events detected with Bare CFEs vs Pt-CFEs. B) Normalized frequency histograms of number of molecules released. C) Normalized frequency histograms of the cube root of number of molecules released may be fit by a gaussian.

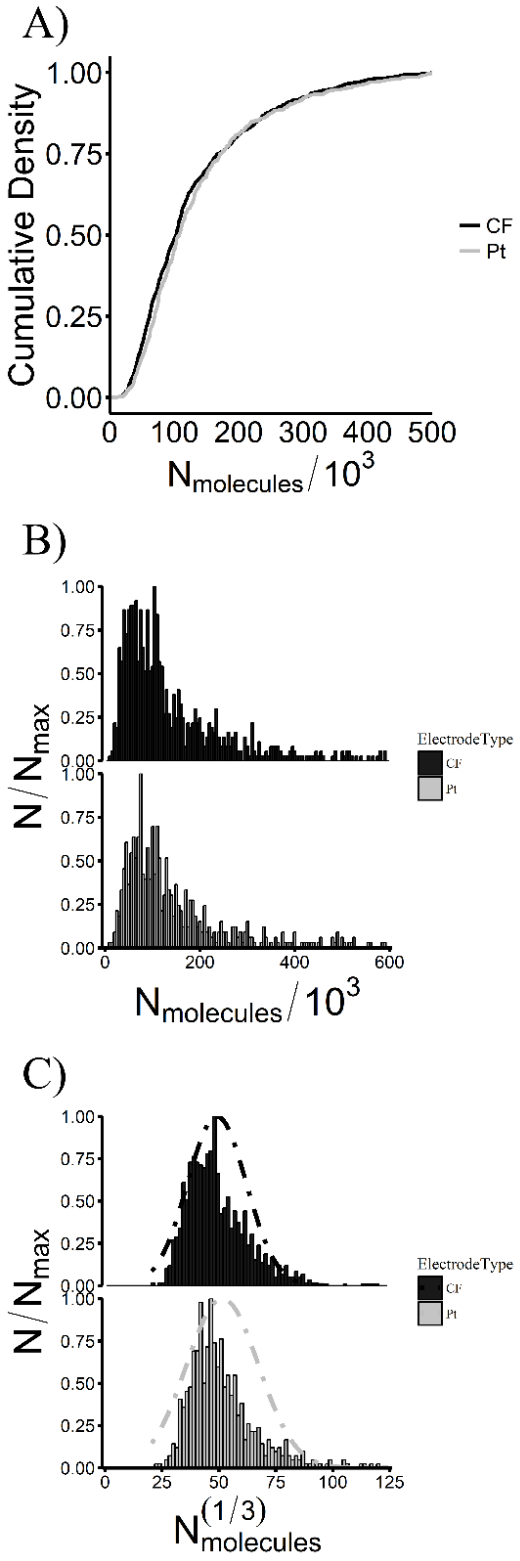

Figure S7. Addition of Au does not change bulk exocytosis properties. A) Average number of events recorded per cell with different probes. B) Average interspike interval (ms) for events recorded with different probes.

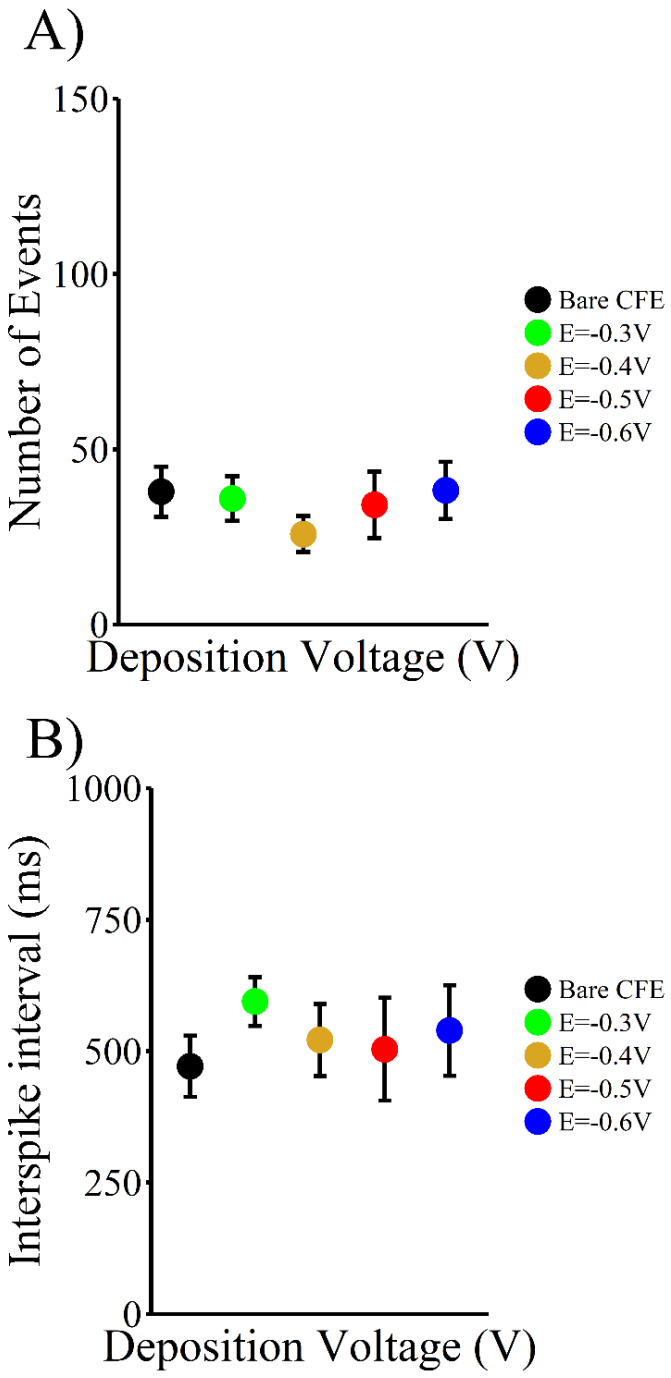

Figure S8. Addition of Au does not change observed bulk exocytosis properties in cells pre-treated with L-DOPA. A) Average number of events recorded per cell with different probes. B) Average interspike interval (ms) for events recorded with different probes.

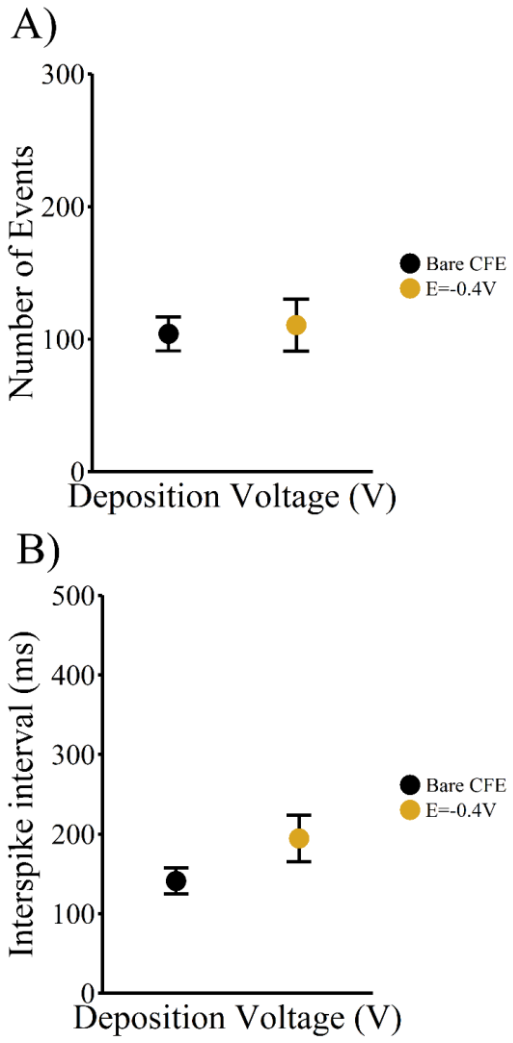

Figure S9. No peaks are detected in the absence of Ca^{2+}. A) unmodified CFE, B) -0.3 V, C) -0.4 V, D) -0.5 V, and E) -0.6 V.