Supplemental Materials

A Cobalt Oxide Carbon Nanotube Composite to Assay Dopamine

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Content: 7 figures showing XPS, CV, Ip and Randles-Sevcik analyses, close-up TEM images of the COOH-MWNT support and CoO/COOH-MWNT composite, and calculation for limit of detection (LOD).

Figure S1 shows the C 1s, O 1s and Co 2p orbitals spectrum from the CoO/COOH-MWNT. The spectrum shows two major peaks at the 284.4 eV (2.5) and 286.9 eV (4.2) positions. The major binding energy (BE) peak at 284.4 eV indicates the presence of sp^2 C-C/or C-H orbital (graphene) in the COOH-MWNTs [1]. The BE peak at 286.9 eV (4.2) position corresponds to the carbon atoms of C-O (COOH group) of COOH-MWNT [2]. The O 1s orbitals show two BE peaks at 531.2 eV (2.3) and 532.8 eV (3.5) (with full-width-at-half-maxima in parentheses) from single- and double-bonded oxygen [3]. The BE peak at 531.2 (2.3) emanates from a –C=O group within the composite [4]. The peak at 532.8 (3.5) eV denotes hydroxyl oxygen [5]. The Co 2p XPS spectrum shows spin orbit coupling. The Co $2p_{1/2}$ and Co $2p_{3/2}$ peaks also have shake-up satellite structures indicating a Co(+2) chemical oxidation state [6].

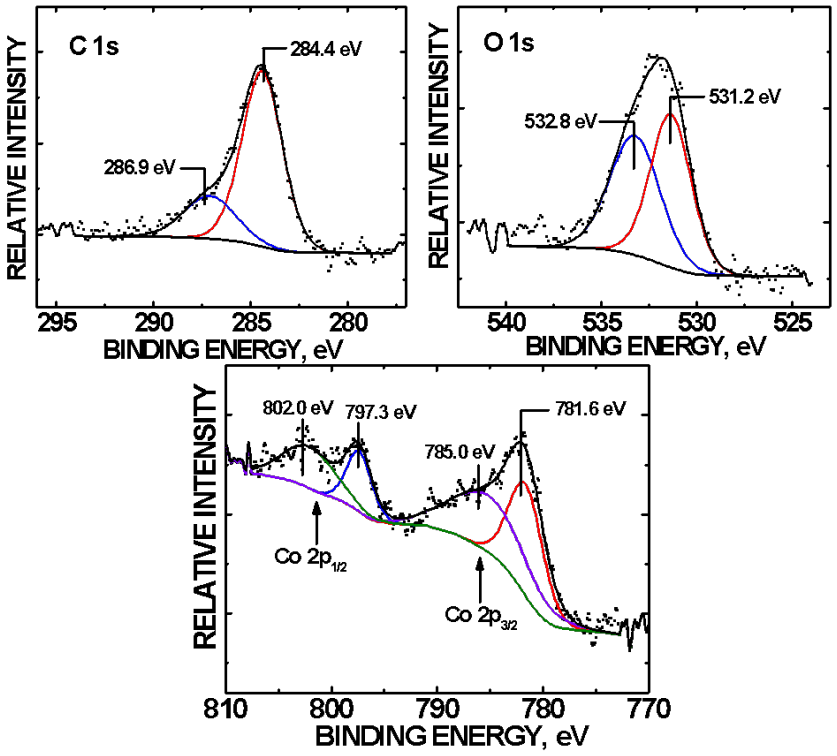


Figure S1: XPS of C 1s, O 1s and Co 2p core levels from CoO/COOH-MWNTs.

The spin orbit coupling doublet splitting (Co $2p_{1/2}$ - Co $2p_{3/2}$) is 797.7–781.8 = 15.9 eV, which is the characteristic of CoO [7-9].

Figure S2A shows CVs at various pH conditions for 100 µM DA. The voltammogram shows a nonlinear relationship in peak current with the change of pH. Figure S2B shows current vs pH in the 1-7 pH range for 100 µM DA. The maximum sensitivity was found at pH 5.0.

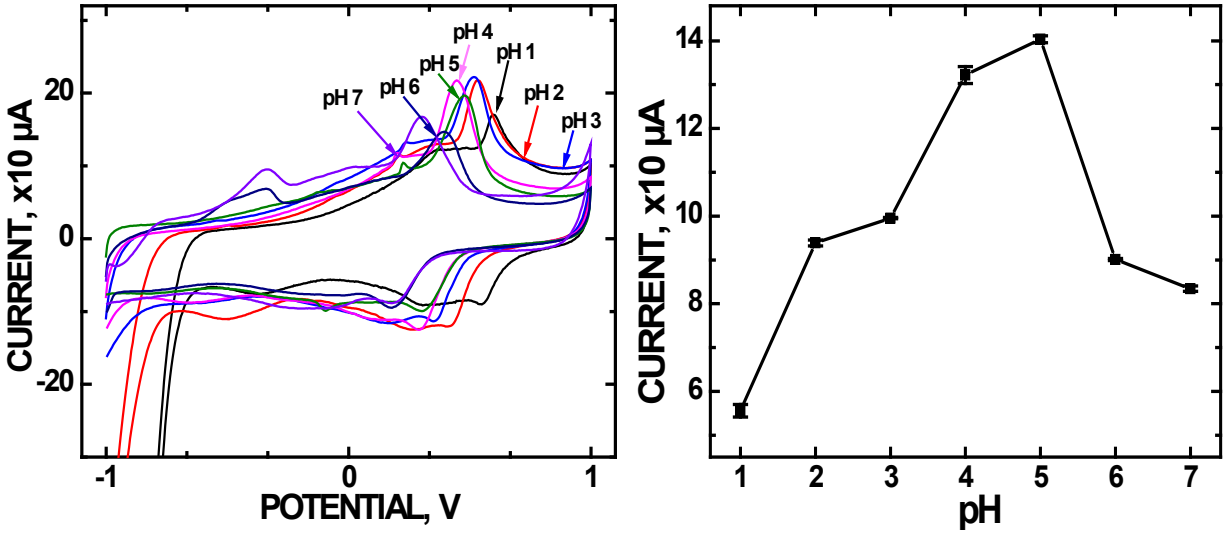


Figure S2: **(A)** A CV of 100 µM dopamine using Nafion/CoO/COOH-MWNT/GCE at various pH; **(B)** Peak current versus pH of 100 µM dopamine. CV currents at each pH condition were extracted at their various, respective peak maxima positions.

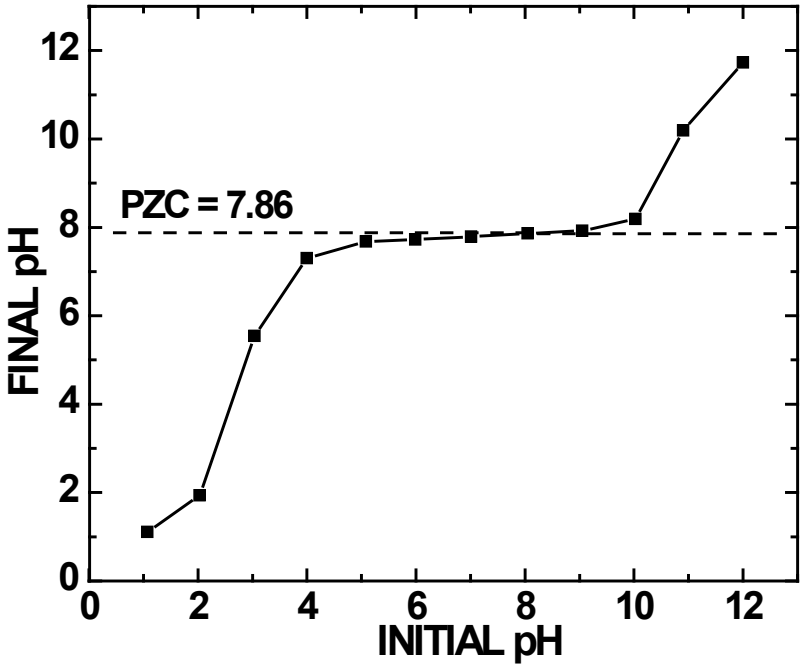


Figure S3: Point-of-Zero-Charge (PZC) measurement of the CoO/COOH-MWNT composite.

Figure S3 shows the measured isoelectric point (Ip) as indicated by the point-of-zero charge (PZC), denoted by the horizontal dashed line. The Ip procedure is based on a technique originally reported by Park and Regalbuto [9] that was more recently modified in our lab to measure the Ip of carbon nanomaterials [10]. The measurement was obtained using the following procedure. Twelve solutions in the range of 1 to 12 were made using dilute aqueous solutions of NaOH and HCl. Aliquots of 1.8 mL were pipetted into polyethylene vials and allowed to equilibrate for 1 hour. The initial pH of each solution was then recorded. Solid samples (2 mg each) were then added to each vial, each of which were capped and shaken with a vortex mixer. After 16 additional hours, allowing for equilibration of protonation/deprotonation, the final pH for each vial was measured using a spear-tip semisolid pH electrode. The plot of final versus initial pH resulted in a plateau denoting the Ip at 7.86.

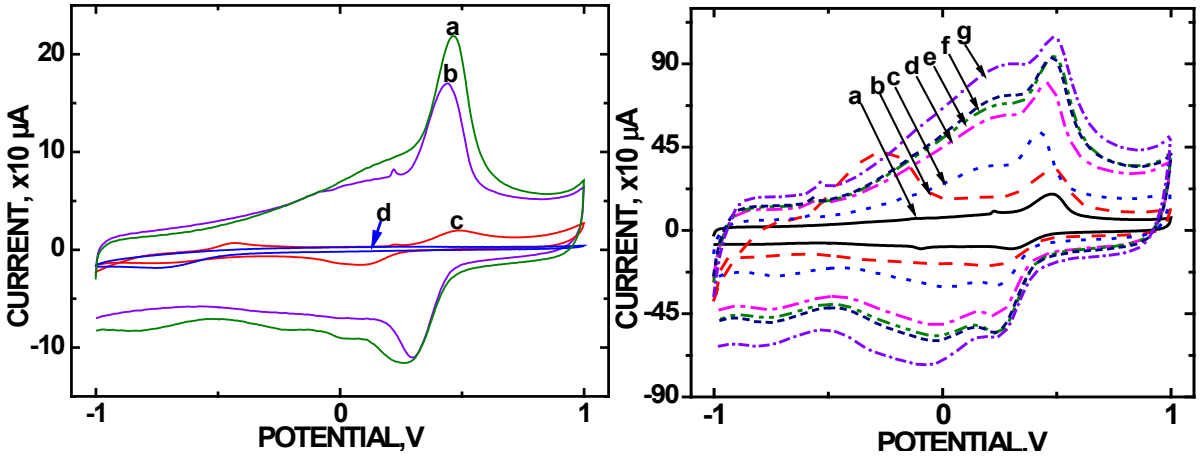


Figure S4: (A) CVs of 100 µM DA using **(a)** CoO/COOH-MWNT /GCE, **(b)** Pure COOH-MWNT/GCE, **(c)** Pure CoO/GCE, and **(d)** GCE; **(B)** CVs of DA at **(a)** 0.13 µg/mm^2, **(b)** 0.25 µg/mm^2, **(c)** 0.38 µg/mm^2, **(d)** 0.51 µg/mm^2, **(e)** 0.64 µg/mm^2, **(f)** 0.76 µg/mm^2, and **(g)** 0.89 µg/mm^2 loadings of the CoO/COOH-MWNT/GCE composite in PBS at pH 7.0 under N_2 atmosphere.

The modified CoO/COOH-MWNT/GCE electrode showed enhanced sensitivity towards dopamine compared to the other types of electrodes which are not modified by CoO particles. The control study for the developed sensor was done using components of materials used in the modified composite. The study shows that the 2 wt % Nafion has no response towards dopamine and pure CoO and COOH-MWNT has a lower sensitivity with compared to the developed 2 wt % Nafion/CoO/COOH-MWNT composite. In addition, the COOH-MWNT/GCE insensitive towards DA concentration; variation in concentration between 10 and 100 µM resulted in the same CV lineshape.

Figure S4 shows cyclic voltammogram for a sequence of different loadings of composite (CoO/COOH-MWNT) with dopamine concentration of 100 µM. The current increases with the variation of composite loading. The maximum sensitivity of the sensor was found at a 0.89 µg/mm^2 loading of the composite.

Figure S5A shows the current vs scan rate plot for 100 µM dopamine concentration. There is a linear relationship was evident spanning the 10 to 100 mV/s scan rates. The current increases with the increase of the square root of the scan rate for the reduction of DA. The plot of reduction current vs the square root of the scan rate yields a linear relationship, indicating a diffusion controlled process on the CoO/COOH-MWNT working electrode surface.

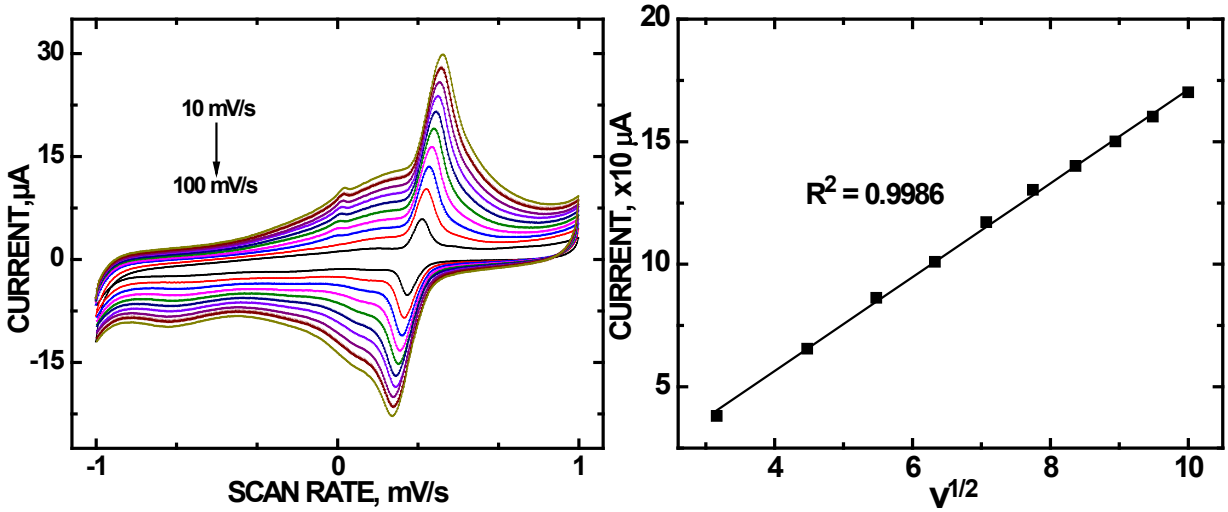


Figure S5: (A) Current versus scan rate for 100 µM dopamine concentration; **(B)** Current versus square root of the scan rates.

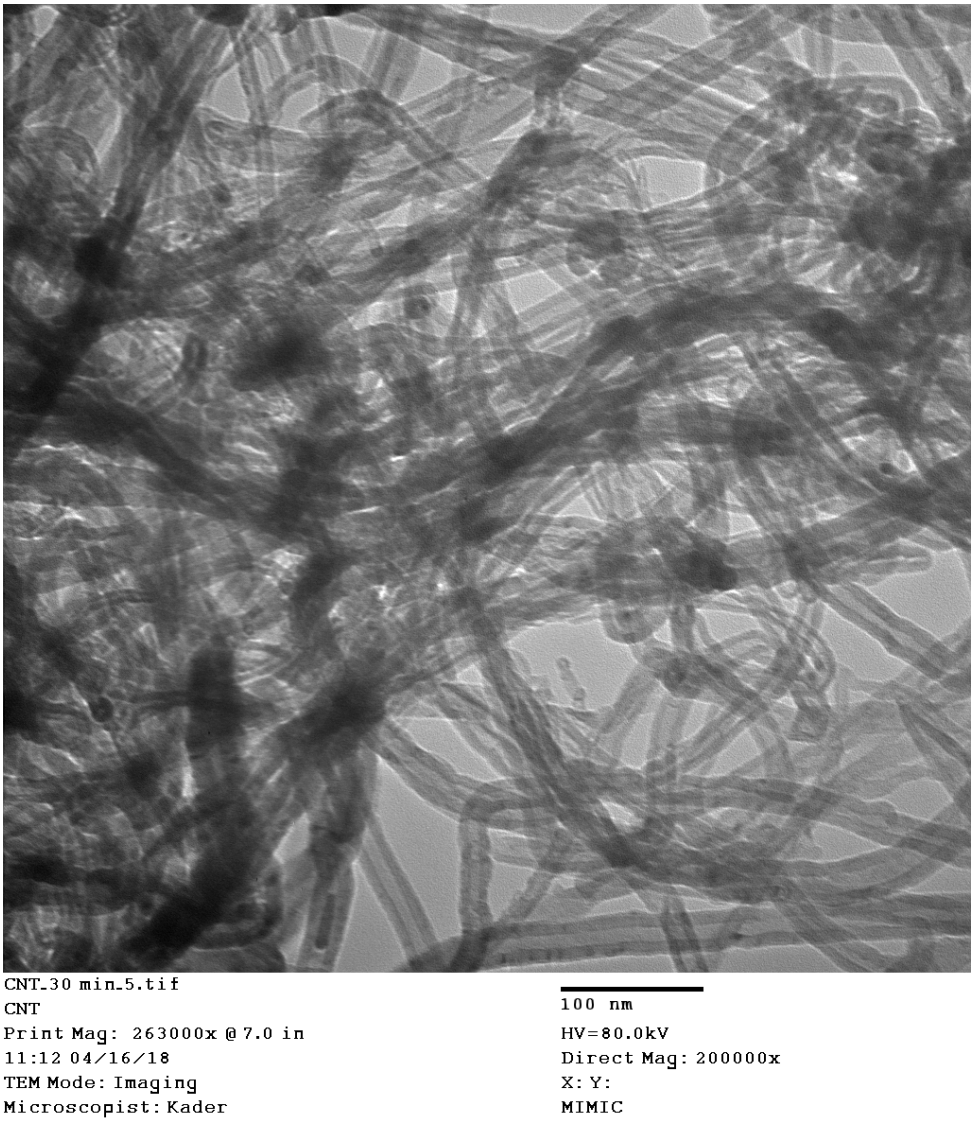


Figure S6: Close-up TEM of 30-minute sonicated CoO/COOH-MWNT composite showing underlying COOH-MWNT support in area without particles (scale bar = 100 nm).

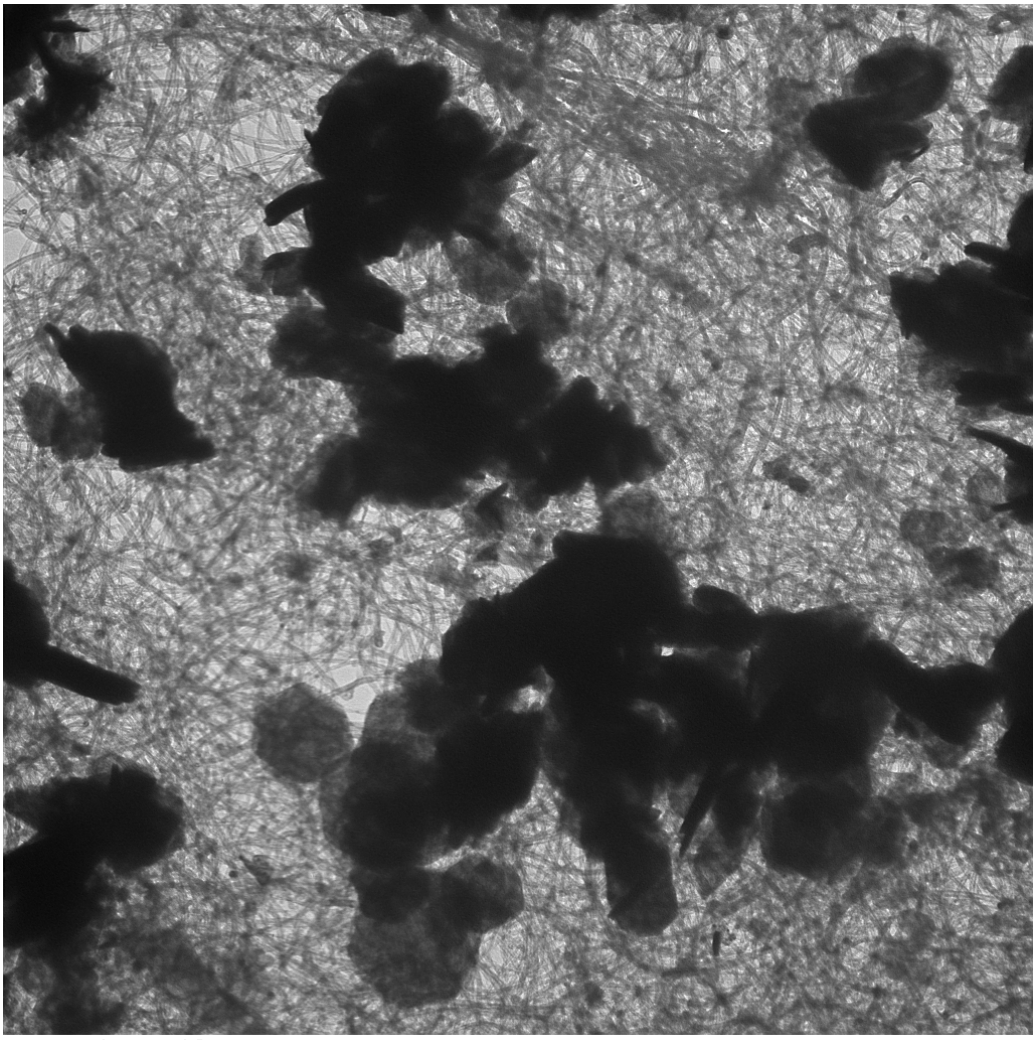
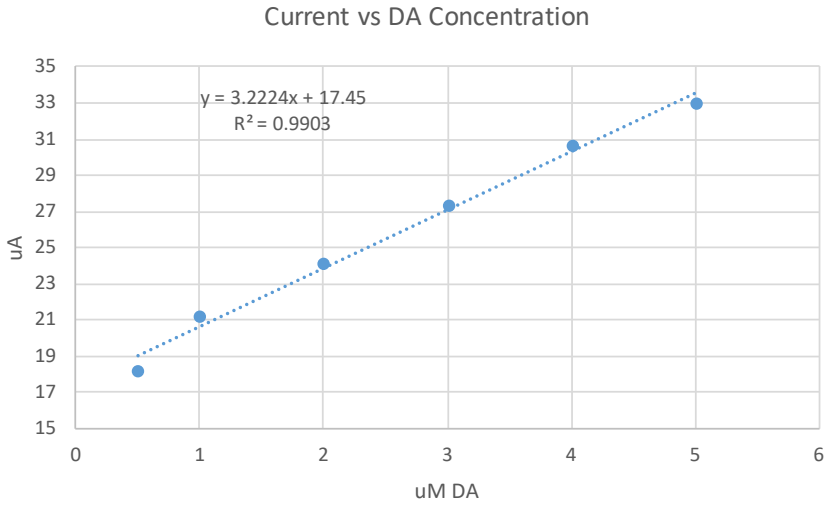


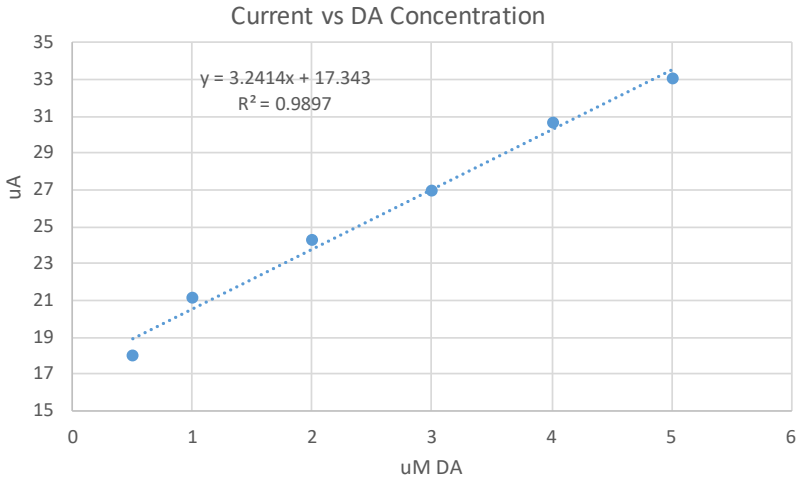
Figure S7: Close-up TEM of 30-minute sonicated CoO/COOH-MWNT composite showing underlying COOH-MWNT support in area with CoO particles (scale bar = 500 nm).

Limit of Detection (LOD) Calculation for DA (1 of 2)

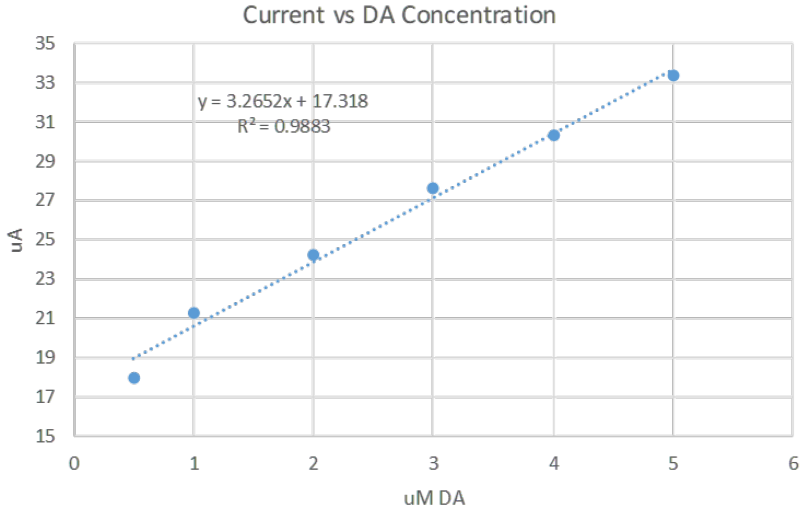


Trial 1						
x (uA)	y (uM)	mx	d_i	d_i^2		
0.5	18.2	1.6112	-0.8612	0.741665	$\Sigma d_i^2 =$	1.551046
1	21.25	3.2224	0.5776	0.333622	$\Sigma d_i^2/(n-2) =$	0.387762
2	24.16	6.4448	0.2652	0.070331	$s_y =$	0.622705
3	27.36	9.6672	0.2428	0.058952	$3s_y/m =$	0.579728
4	30.63	12.8896	0.2904	0.084332		
5	33.05	16.112	-0.512	0.262144		

Limit of Detection (LOD) Calculation for DA (2 of 2)



Trial 2						
x (uA)	y (uM)	mx	d_i	d_i^2		
0.5	18.09	1.6207	-0.8737	0.763352	Σd_i^2 =	1.657302
1	21.15	3.2414	0.5656	0.319903	$\Sigma d_i^2/(n-2)$ =	0.414326
2	24.31	6.4828	0.4842	0.23445	s_y =	0.643681
3	27	9.7242	-0.0672	0.004516	$3s_y/m$ =	0.599256
4	30.66	12.9656	0.3514	0.123482		
5	33.09	16.207	-0.46	0.2116		



summary of results

LOD (Trial 1) = $3s_y/m$ =	0.57973
LOD (Trial 2) = $3s_y/m$ =	0.59926
LOD (Trial 3) = $3s_y/m$ =	0.64377
average =	0.60759
STD =	0.03282

Trial 3						
x (uA)	y (uM)	mx	d_i	d_i^2		
0.5	17.95	1.6326	-1.0006	1.0012	Σd_i^2 =	1.912672
1	21.25	3.2652	0.6668	0.444622	$\Sigma d_i^2/(n-2)$ =	0.478168
2	24.20	6.5304	0.3516	0.123623	s_y =	0.691497
3	27.57	9.7956	0.4564	0.208301	$3s_y/m$ =	0.643772
4	30.25	13.0608	-0.1288	0.016589		
5	33.30	16.326	-0.344	0.118336		

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