

*Supporting Information for:*

***In situ* Detection of Dopamine using Nitrogen Incorporated Diamond Nanowire  
Electrode**

Jayakumar Shalini,<sup>a</sup> Kamatchi Jothiramalingam Sankaran,<sup>a</sup> Chung-Li Dong,<sup>b</sup>  
Chi-Young Lee,\*<sup>a</sup> Nyan-Hwa Tai,<sup>a</sup> and I-Nan Lin\*<sup>c</sup>

<sup>a</sup>Department of Material Science and Engineering, National Tsing-Hua University,  
Hsinchu 300, Taiwan, R.O.C

<sup>b</sup>Scientific Research Division, National Synchrotron Radiation Research Center,  
Hsinchu 300, Taiwan, R.O.C

<sup>c</sup>Department of Physics, Tamkang University, New-Taipei 251, Taiwan, R.O.C

**Figure Caption:**

**Fig. S1.** (a, b and c) shows cyclic voltammetric  $i$ - $E$  curves (no iR correction) of DNW film electrodes at  $T_S$  for the redox analytes: a) 0.1 mM  $\text{Fe}(\text{CN})_6^{3/-4}$ , b) 0.1 mM  $\text{Ru}(\text{NH}_3)_6^{+2/+3}$  and c) 0.1 mM 4- tert-butylcatechol in 0.1 M KCl.

**Fig. S2.** (a, b and c) Differential pulse voltammetry curves graphite, glassy carbon and boron doped diamond electrodes in a solution containing 0.33 mM AA + 0.033 mM DA + 0.033 mM UA.

**Fig. S3.** Differential pulse voltammetry curves diamond nanowire and boron doped diamond electrodes in a solution containing 0.33 mM AA + 0.033 mM DA + 0.033 mM UA.

**Fig. S4.** (a, and b) Differential pulse voltammetry curves for fresh and prolonged usage of (a) diamond nanowire and (b) boron doped diamond electrode in a solution containing 0.33 mM AA + 0.033 mM DA + 0.033 mM UA.

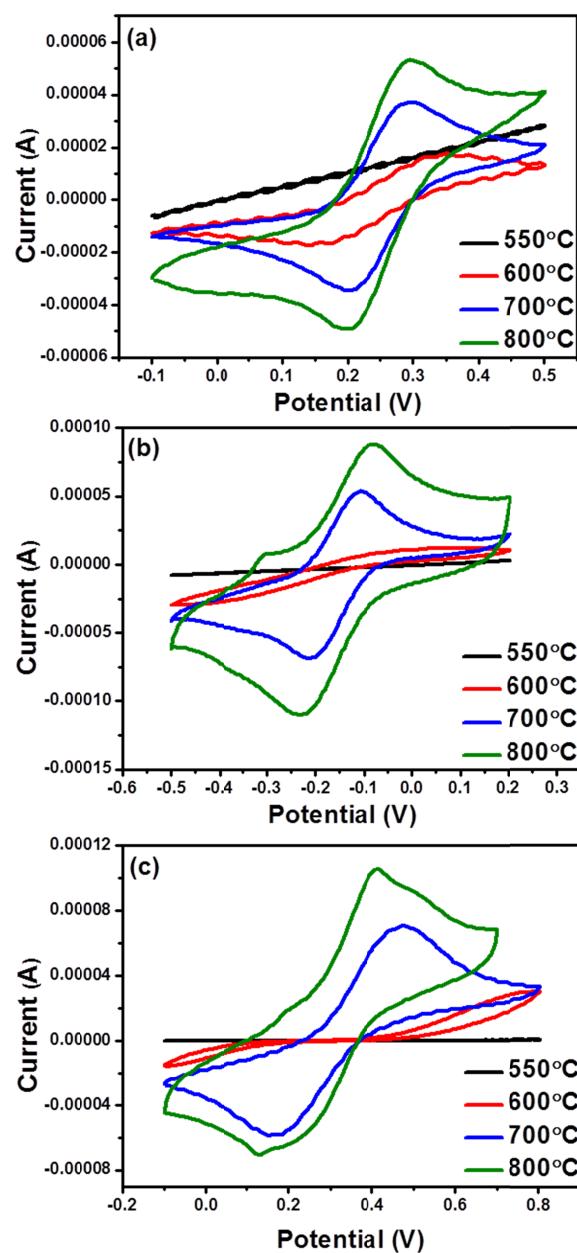
**Table Caption:**

**Table S1.** Summary of the oxidation peak currents and potentials for the detection of AA, DA and UA using diamond nanowire film electrodes grown at 550-800 °C electrodes without any additional modification in cyclic voltammograms.

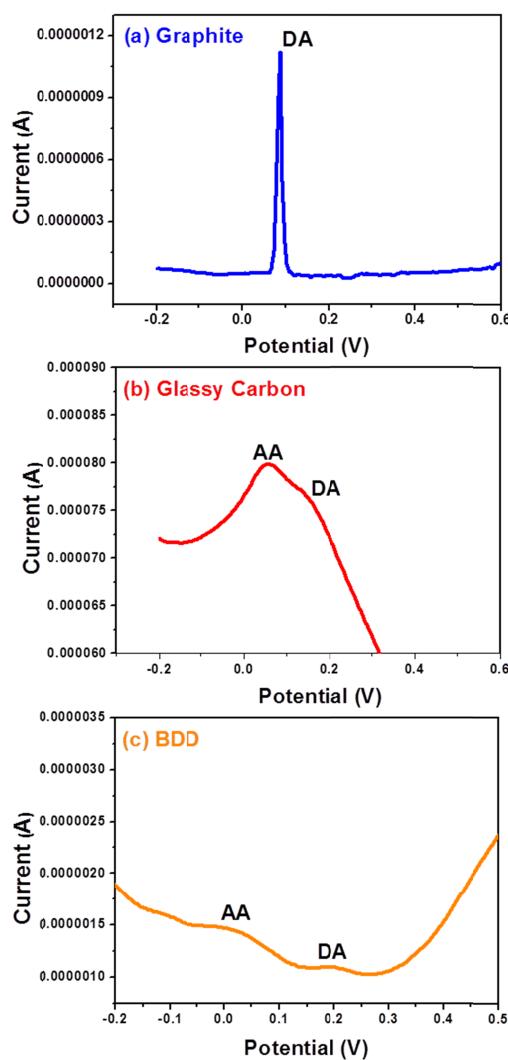
**Table S2.** Summary of the dynamic range and limit of detection of DA in the presence of interference (AA and UA) obtained by differential pulse voltammetry using diamond nanowire film electrodes.

**Table S3.** Summary of previously published results for the detection of AA, UA and DA using cyclic voltammetry with different electrodes.

**Table S4.** Summary of previously published results for the detection of DA using amperometric measurements with different electrodes.



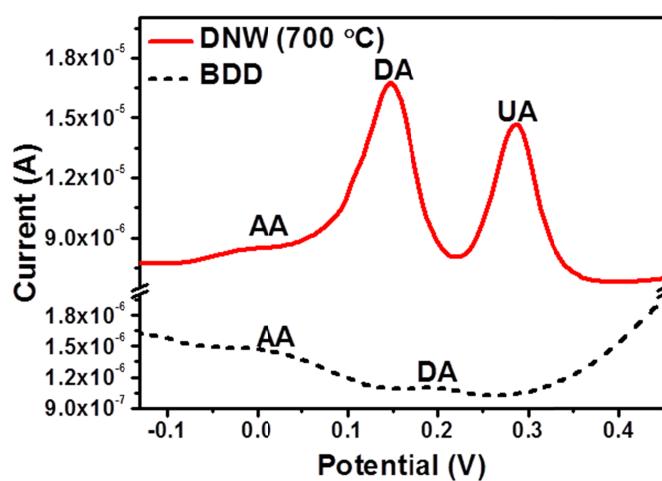
**Fig. S1.** (a, b and c) shows cyclic voltammetric  $i$ - $E$  curves (no iR correction) of DNW film electrodes at  $T_S$  for the redox analytes: a) 0.1 mM  $\text{Fe}(\text{CN})_6^{3/-4}$ , b) 0.1 mM  $\text{Ru}(\text{NH}_3)_6^{+2/+3}$  and c) 0.1 mM 4- tert-butylcatechol in 0.1 M KCl.



**Fig. S2.** (a, b and c) Differential pulse voltammetry curves graphite, glassy carbon and boron doped diamond electrodes in a solution containing 0.33 mM AA + 0.033 mM DA + 0.033 mM UA.

### Antifouling Effect:

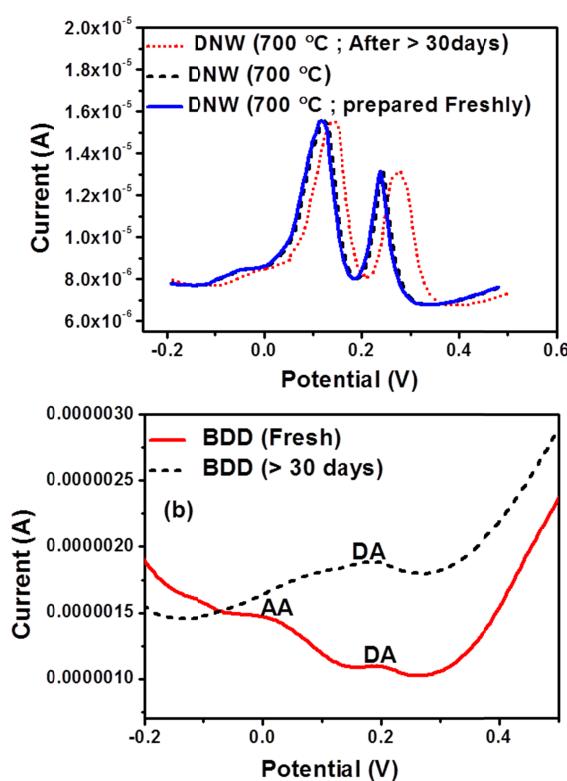
The diamond nanowire (DNW) films deposited at substrate temperature ( $T_s$ ) of about 700 °C and the boron doped diamond (BDD) film electrodes are compared which clearly shows that the non-surface modified DNW films electrode (solid line) do not undergo electrode fouling effect and thus we obtain well separated voltammetric peak for AA, DA and UA. However BDD electrode (dotted line) shows lack in sensitivity for the DA detection in the ternary mixture due to fouling effect.



**Fig. S3.** Differential pulse voltammetry curves diamond nanowire and boron doped diamond electrodes in a solution containing 0.33 mM AA + 0.033 mM DA + 0.033 mM UA.

### Reproducibility:

Fig.S4 (a) shows the cyclic voltammograms of the oxidation of 0.33 mM AA + 0.033 mM DA + 0.033 mM UA at the recently prepared DNW films ( $T_S = 700\text{ }^\circ\text{C}$ ) electrode, fresh DNW film and at the same electrode after > 30 days of contact with the laboratory air. A well-separated peak was obtained even after 30 days of storage, with a small positive shift (about 13 mV for DA and 22 mV for UA) in the oxidation peak, whereas recently prepared DNW electrode shows better reproducibility in terms of selectivity. On the other hand, the BDD electrode underwent rapid deactivation during the oxidation [Figure S4 (b)]. For example, Fujishima et al. observed an anodic shift of the DA oxidation peak by approximately 80 mV due to deactivation of untreated BDD electrode.<sup>1</sup>



**Fig. S4.** (a, and b) Differential pulse voltammetry curves for fresh and prolonged usage of (a) diamond nanowire and (b) boron doped diamond electrode in a solution containing 0.33 mM AA + 0.033 mM DA + 0.033 mM UA.

**Table S1.** Summary of the oxidation peak currents and potentials for the detection of AA, DA and UA using diamond nanowire film electrodes grown at 550–800 °C electrodes without any additional modification in cyclic voltammograms.

Analyte	DNW film Electrodes (°C)	I <sub>pa</sub> (μA)	E <sub>pa</sub> (V)
AA	550	19.06	0.475
	600	12.10	0.216
	700	29.86	0.035
	800	74.70	0.269
DA	550	50.67	0.245
	600	73.39	0.240
	700	90.89	0.235
	800	77.76	0.265
UA	550	76.54	0.553
	600	36.78	0.338
	700	91.62	0.367
	800	92.62	0.421

**Table S2.** Summary of the dynamic range and limit of detection of DA in the presence of interference (AA and UA) obtained by differential pulse voltammetry using diamond nanowire film electrodes.

Electrode	DA dynamic range ( $\mu\text{M}$ )	DA Limit of detection ( $\mu\text{M}$ )	AA (mM)	UA (mM)	Ref
COOH-BDD electrodes	0–30	0.1	0.5	-	2
Attachment of gold nanoparticles to GC electrode	20–145	-	1.5	-	3
poly ( <i>p</i> -nitrobenzenazo resorcinol)modified GC electrode	5–25	0.39	1.1	0.13	4
Poly (Eriochrome Black T) Film Modified Graphite Pencil Electrode	$0.1\text{--}0.3 \times 10^{-3}$	0.08	-	$1 \times 10^{-3}$	5
DNW film (700 °C)	0.5–500	0.34	0.5	0.005	This work

**Table S3.** Summary of previously published results for the detection of AA, UA and DA using cyclic voltammetry with different electrodes.

Electrode	Scan rate (V/s)	Reference electrode	Surface area (cm <sup>2</sup> )	Current (μA)			Current density (μA/cm <sup>2</sup> )			Ref
				AA	DA	UA	AA	DA	UA	
<b>BDD/Gold Nanoparticle/</b>										
Polyelectrolyte-coated Polystyrene Colloids	0.5	SCE	0.07	-	-	-	-	-	-	6
Carbon ionic liquid electrode	0.5	Ag/AgCl	0.18	3.80 ( $1.25 \times 10^{-3}$ M)	4.51 ( $1.25 \times 10^{-3}$ M)	14.92 ( $1.25 \times 10^{-3}$ M)	21.11	25.05	82.88	7
Carbon paste electrode	0.5	Ag/AgCl	0.18	3.5	4.21	5.20	19.44	23.38	28.88	8
Nitrogen incorporated Nanodiamond film	1.0	Ag/AgCl	0.32	-	-	-	-	-	-	9
MWCNT/GCE	0.05	Ag/AgCl	0.07	-	0.7 (0.05 mM)	-	-	10	-	10
Pt-MWCNTs/GCE	0.05	Ag/AgCl	-	22 (0.5 mM)	60 (0.5 mM)	155 (0.5 mM)	-	-	-	11
DNW film (700 °C)	0.05	Ag/AgCl	0.186	29 (1 mM)	91 (1 mM)	91 (1 mM)	161.1	505.6	505.6	This work

**Table S4.** Summary of previously published results for the detection of DA using amperometric measurements with different electrodes.

Electrode	Dynamic range		Limit of detection	Ref
	( $\mu$ M)	DA		
Oxygen-terminated BDD	1–70; 0.1–1		0.05	12
tyrosinase-modified BDD	5–120		1.3	13
Overoxidized polypyrrole (OPPy)-modified BDD electrodes	0.0005–100		0.0001	14
Pt/Graphene/GCE	0.03–8.13		0.03	15
GONR(200 W)/GCE	0.15–12.2		0.08	16
Diamond nanowire film (700 °C)	0.5–500		0.36	<b>This work</b>

**Reference:**

1. A. Fujishima, T. N. Rao, E. Popa, B.V. Sarada, I. Yagi and D.A. Tryk, *Journal of Electroanalytical Chemistry*, 1999, **473**, 179.
2. T. Kondo, Y. Niwano, A. Tamura, J. Imai, K. Honda, Y. Einaga, D. A. Tryk, A. Fujishima and T. Kawai, *Electrochimica Acta*, 2009, **54**, 2312.
3. L. Zhang and X. Jiang, *Journal of Electroanalytical Chemistry*, 2005, **583**, 292.
4. X. Lin, Y. Zhang, W. Chen and P. Wu, *Sensors and Actuators B*, 2007, **122**, 309.
5. U. Chandra, B. E. K. Swamy, O. Gilbert, S. Reddy and B. S. Sherigara, *American Journal of Analytical Chemistry*, 2011, **2**, 262.
6. B. M. Wei, L. G. Sun, Z. Y. Xie, J. F. Zhii, A. Fujishima, Y. Einaga, D.G. Fu, X. M. Wang and Z.Z. Gu, *Adv. Funct. Mater*, 2008, **18**, 1414.
7. A. Safavi, N. Maleki, O. Moradlou and F. Tajabadi, *Analytical Biochemistry*, 2006, **359**, 224.
8. S. C. Balasoiu, R. S. Staden, J. F. V. Staden, S. Pruneanu and G. L. Radu, *Analytica Chimica Acta*. 2010, **668**, 201.
9. S. Raina, W. P. Kang and J. L. Davidson, *Diamond & Related Materials*, 2009, **18**, 574.
10. Z. A. Alothman, N. Bukhari, S. M. Wabaidur and S. Haider, *Sensors and Actuators B*, 2010, **146**, 314.
11. Z. Dursun and B. Gelmez, *Electroanalysis*, 2010, **22**, 1106.
12. Y. Zhou and J. Zhi, *Talanta*, 2009, **79**, 1189.
13. Y. L. Zhou, R. H. Tian and J. Zhi, *Biosensors and Bioelectronics*, 2007, **22**, 822.
14. H. Olivia, B. V. Sarada, D. Shin, T. N. Rao and A. Fujishima, *Analyst*, 2002, **127**, 1572.
15. C. L. Sun, H. H. Lee, J. M. Yang and C. C. Wu, *Biosensors & Bioelectronics*, 2011, **26**, 3450.
16. C. L. Sun, C. T. Chang, H. H. Lee, J. Zhou, J. Wang, T. K. Sham, W. F. Pong, *ACS Nano*. 2011, **5**, 7788.