Supporting information for

Electrogenerated chemiluminescence with peroxydisulfate as a coreactant using boron doped diamond electrodes

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1. Characterization of boron-doped diamond (BDD) electrodes: Raman spectroscopy, and scanning electron microscopy (SEM).

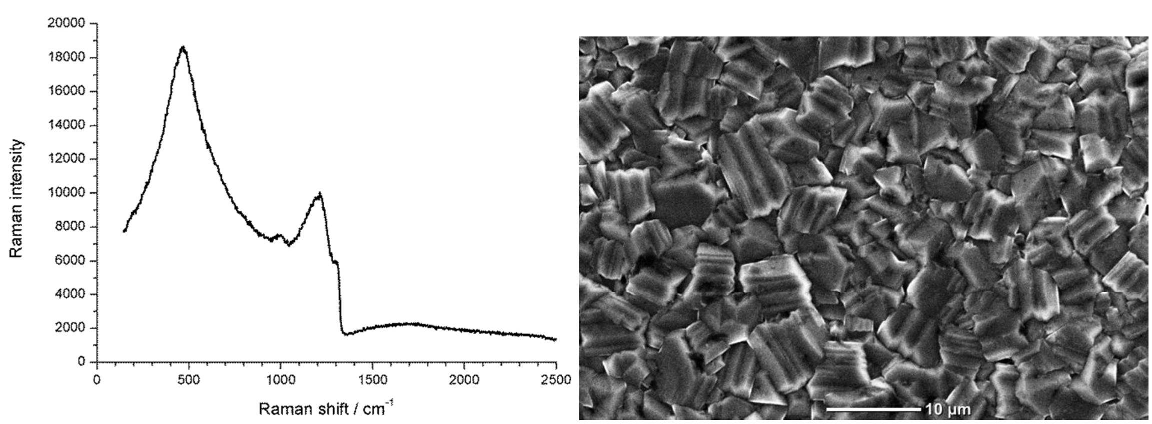

Figure S1. Raman spectra and SEM micrograph of BDD electrode.

The BDD electrode used throughout the ECL experiments is 1% B/C. The high boron-doped diamond exhibits a phonon line (Fano resonance) as a shoulder peak around 1300 cm^{-1}. Non-diamond carbon results in a broad peak at 1600-1700 cm^{-1}.[1,2] The SEM image of the BDD shows the (111) facet as predominant, with crystals from 3 to 5 µm. The B concentration is ≈ $2\times10^{21}/cm^3$, therefore BDD shows metallic conductivity.[1]
A detailed electrochemical characterization of BDD electrode, the same as used in this work, can be found in Ref. 3 and 4.

2. ECL at GC for higher concentration of $Ru(bpy)_3^{2+}$ and $S_2O_8^{2-}$.

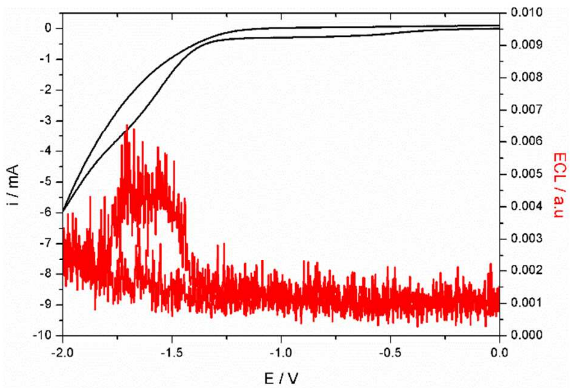

Figure S2. CV (black) and ECL (red) of GC for 50 µM $Ru(bpy)_3^{2+}$ and 500 µM $S_2O_8^{2-}$ in 200 mM PB. Scan rate 100 mV/s and pH 6.8.

3. ECL stability at BDD.

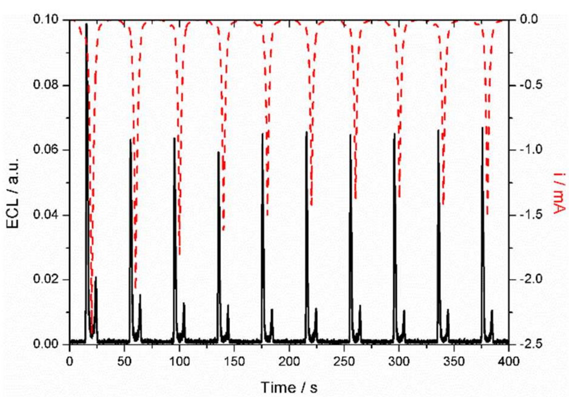

Figure S3. ECL (black) and CV (red) at BDD for 10 µM $Ru(bpy)_3^{2+}$ and 100 µM $S_2O_8^{2-}$ in 200 mM PB. Scan rate 100 mV/s and pH 6.8.

4. ECL spectra.

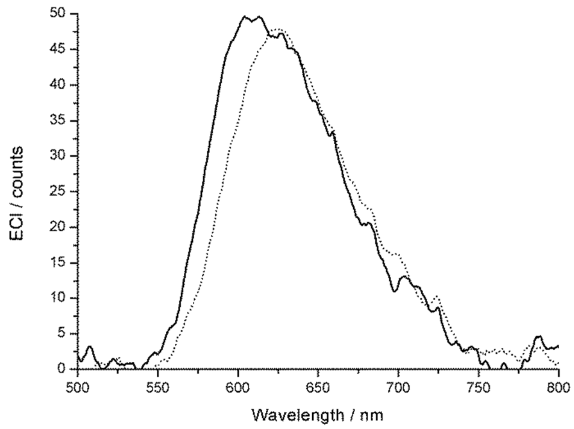

Figure S4. Comparison of ECL spectra at selected potentials from Figure 3. Full line: -1.6 V. Dotted line: -1.7 V.

5. Peroxydisulfate calibration curve.

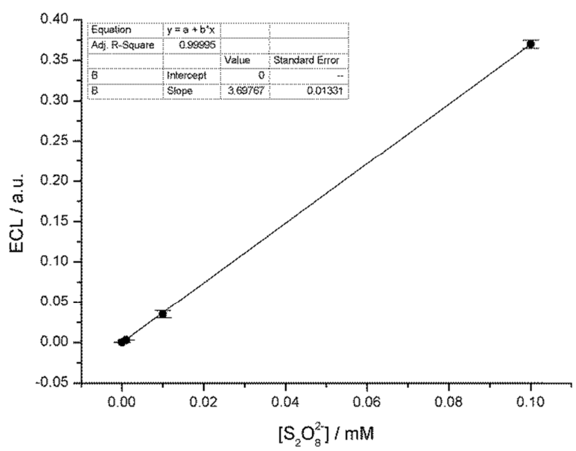

Figure S5. Linear regression for peroxydisulfate calibration from 1 to 100 μM (background subtracted). Limit of Detection (S/N=3) = 0.5 μM, Limit of Quantification (S/N=10) = 1 μM.

6. pH effect on ECL emission and current.

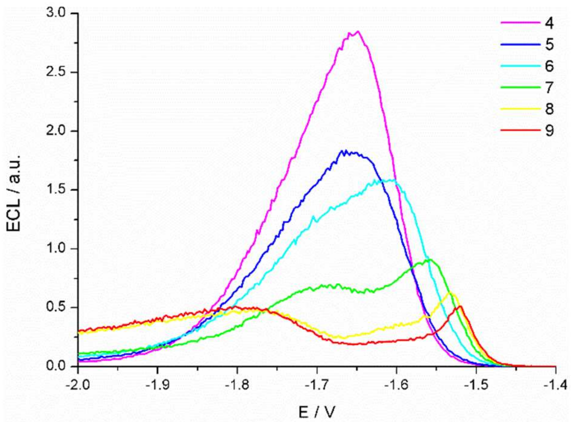

Figure S6. ECL by cyclic voltammetry for 10 μM $Ru(bpy)_3^{2+}$ and 1 mM $S_2O_8^{2-}$ in 200 mM PB, for pH 9 to 4. Scan rate 100 mV/s.

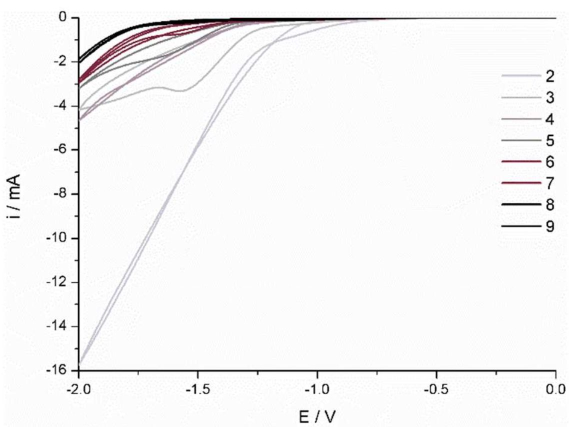

Figure S7. Cyclic voltammetry for 10 μM $Ru(bpy)_3^{2+}$ and 100 μM $S_2O_8^{2-}$ in 200 mM PB, for pH 9 to 2. Scan rate 100 mV/s.

7. References.

(1) Macpherson, J. V. A practical guide to using boron doped diamond in electrochemical research. *Phys. Chem. Chem. Phys.* **2015**, *17*, 2935-2949.

(2) Cobb, S. J.; Ayres, Z. J.; Macpherson, J. V. Boron Doped Diamond: A Designer Electrode Material for the Twenty-First Century. *Annu. Rev. Anal. Chem.* **2018**, *11*, 463-484.

(3) Kasahara, S.; Natsui, K.; Watanabe, T.; Yokota, Y.; Kim, Y.; Iizuka, S.; Tateyama, Y.; Einaga, Y. Surface Hydrogenation of Boron-Doped Diamond Electrodes by Cathodic Reduction. *Anal. Chem.* **2017**, *89*, 11341-11347.

(4) Xu, J.; Natsui, K.; Naoi, S.; Nakata, K.; Einaga, Y. Effect of doping level on the electrochemical reduction of CO_2 on boron-doped diamond electrodes. *Diam. Relat. Mater.* **2018**, *86*, 167-172.