

Supplementary Information

Co-reactant-on-Demand ECL: Electrogenenerated Chemiluminescence by the in Situ Production of $S_2O_8^{2-}$ at Boron-Doped Diamond Electrodes

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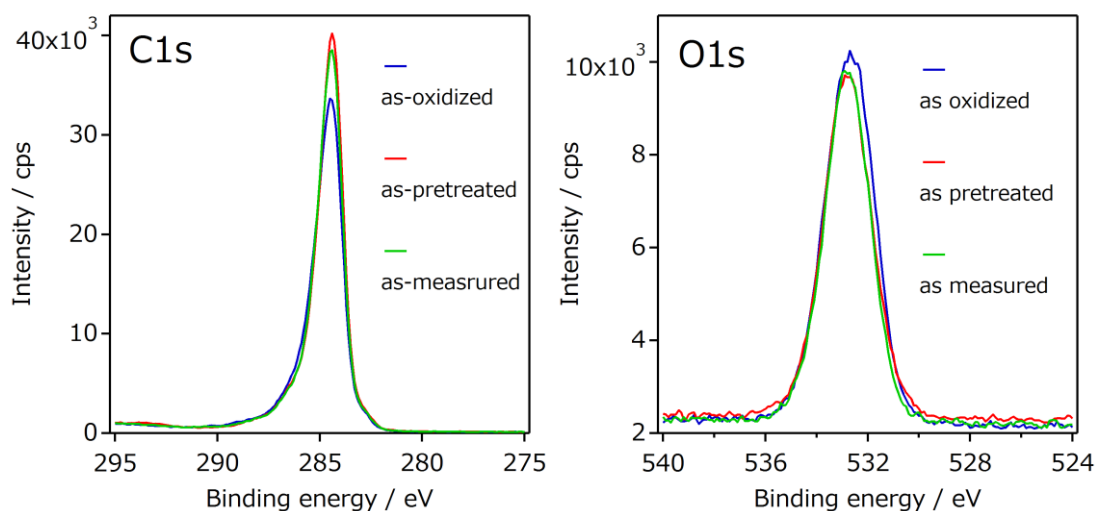


Figure S1. XPS analysis (C1s and O1s) of as-oxidized BDD (potential scanned from 0 V to 3 V for 10 cycles, 300 mV/s), as-pretreated BDD (potential range -3 V to 3 V and 0 V to -3 V each for 10 cycles, 300 mV/s), and as-measured BDD (potential scanned from 0 V to 3 V to -2 V , 100 mV/s). All electrochemical measurement conducted in 0.1 M KClO_4 solution.

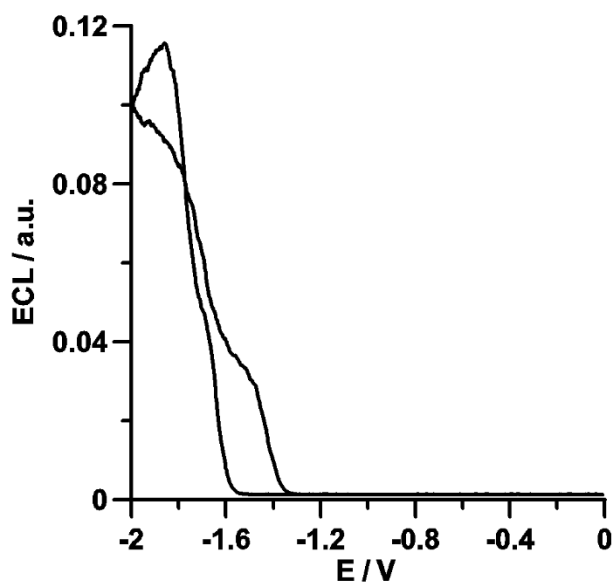


Figure S2. ECL of $1\text{ mM Na}_2\text{S}_2\text{O}_8$ and $5\text{ }\mu\text{M Ru}(\text{bpy})_3\text{Cl}_2$ in water : acetonitrile 50:50, from 0 V to -2.0 V . Scan rate 100 mV/s , potential referred to Ag/AgCl (KCl saturated) at room temperature. PMT bias 1250 V , amplification 000.0 nA .

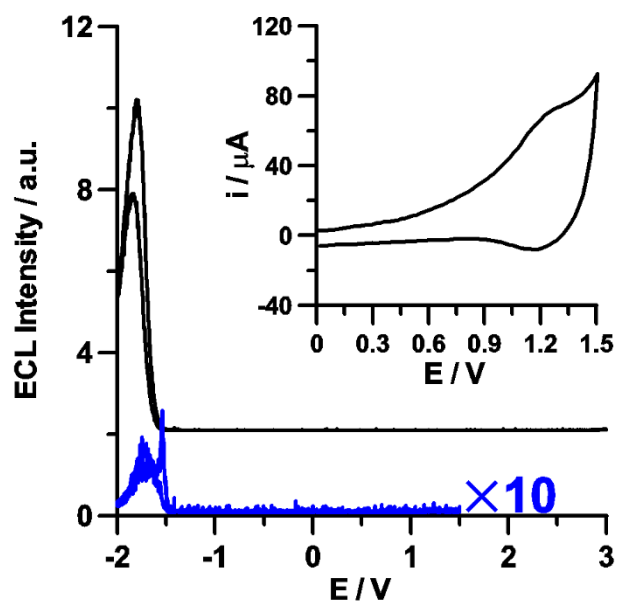


Figure S3. ECL of 0.1 M Na_2SO_4 and 5 μM $\text{Ru}(\text{bpy})_3\text{Cl}_2$ in water solvent at different potential range: 3 V to -2 V (black), 1.5 V to -2 V (blue). Scan rate 100 mV/s, potential referred to Ag/AgCl (KCl saturated) at room temperature. PMT bias 750 V, amplification 000.0 nA. The curves are shifted for clarity.

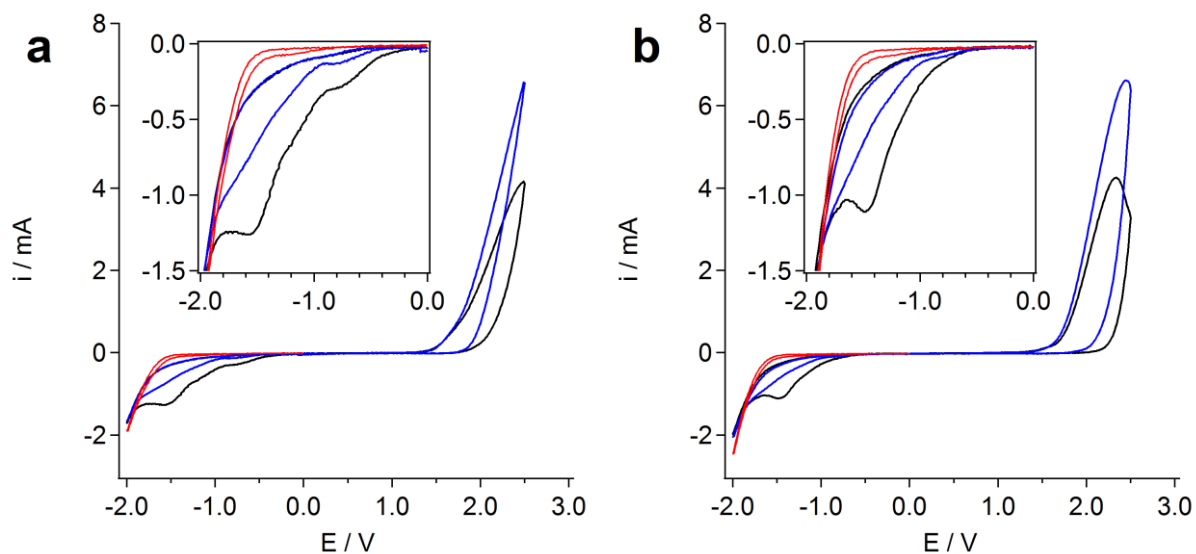
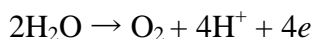
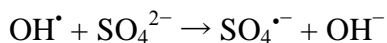


Figure S4. Cyclic voltammograms in a) 0.1 M KClO_4 and b) 0.1 M Na_2SO_4 aqueous solutions. Potential scanned from 0 V to -2.0 V (red), 0 V to 3.0 V to -2.0 V (black), and 0 V to 3.0 V to -2.0 V with pause at 0 V for 3 min before going to -2.0 V (blue). Scan rate 100 mV/s, potential referred to Ag/AgCl (KCl saturated) at room temperature. The solution was bubbled with N_2 gas before measurement.

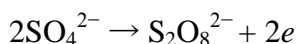
Reaction in KClO_4 and Na_2SO_4



Reactions in Na_2SO_4



Total reaction:



The onset potential for ORR is appeared differently in KClO_4 and Na_2SO_4 solutions. This is possibly because the pH at the electrode surface is different between both solutions after positive scan.

It is reported that the ORR at BDD electrodes start at more positive potential at lower pH.^{1,2} As shown in the reaction above, in the KClO_4 solution the surface pH is relatively decreased due to the production of H^+ from the water oxidation reaction. On the other hand, in the Na_2SO_4 solution, even though the current is similar to KClO_4 solution, the production of H^+ is relatively lower since the oxidation of sulfate ion also occurs without variation of H^+ .

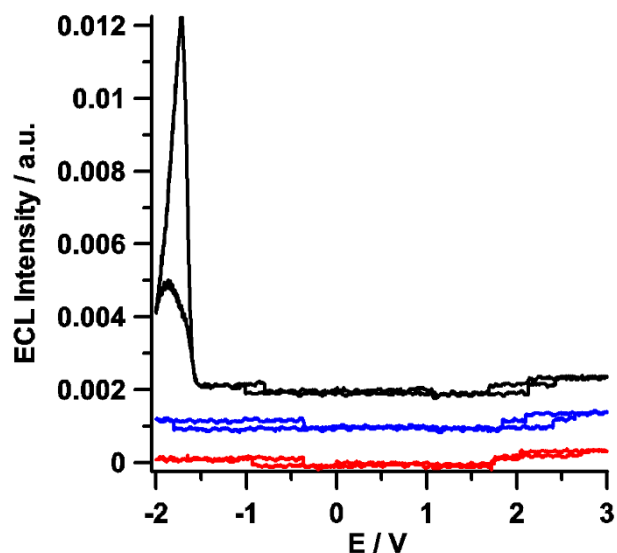


Figure S5. Comparison between BDD (black), GC (blue), and Pt (red) electrodes with $5 \mu\text{M}$ $\text{Ru}(\text{bpy})_3\text{Cl}_2$ and 0.1 M Na_2SO_4 in water solution from 3.0 V to -2.0 V . Scan rate 100 mV/s , potential referred to Ag/AgCl (KCl saturated) at room temperature. PMT bias 750 V , amplification $000.0 \mu\text{A}$. The curves are shifted for clarity.

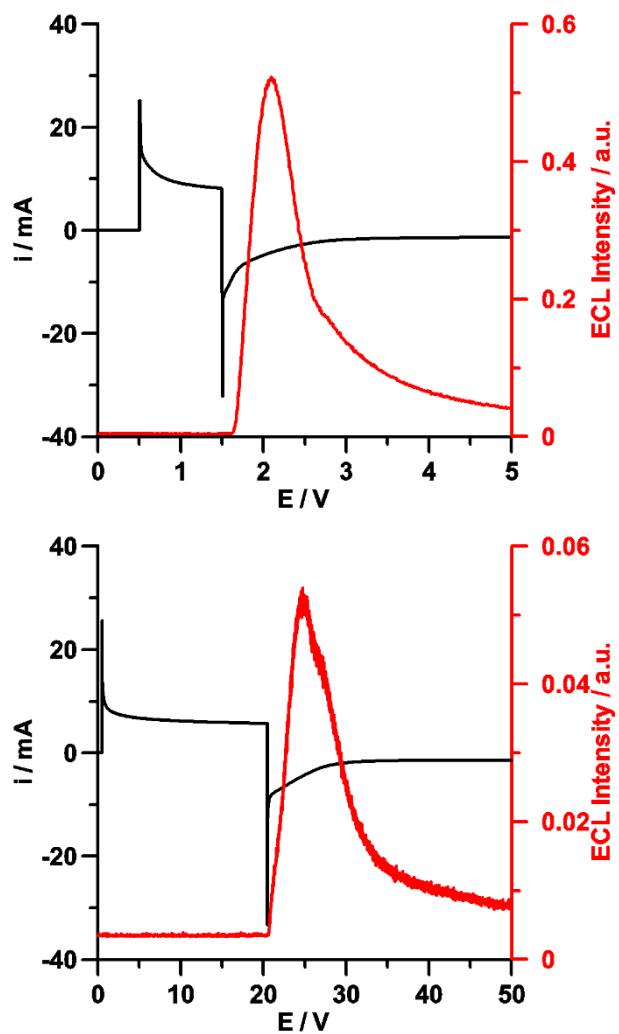


Figure S6. Current and ECL transients with 5 μ M Ru(bpy)₃Cl₂ and 0.1 M Na₂SO₄ in water solution for two different t_{ox} , i.e. 1 s and 20 s; first step 3.0 V, second step -2.0 V. PMT bias 750 V, amplification 00.0 μ A.

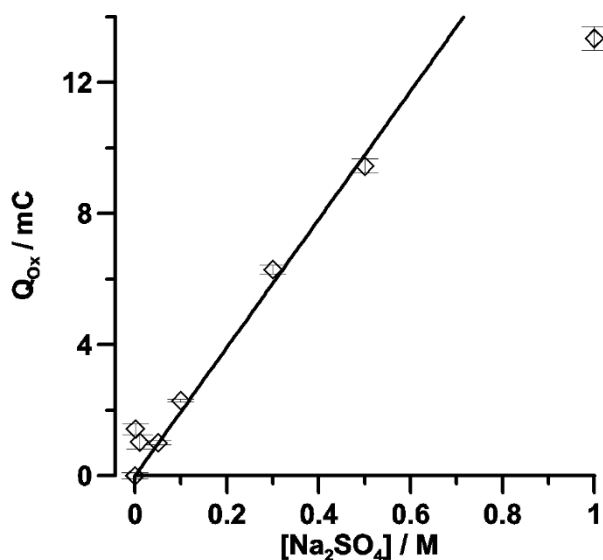


Figure S7. Integrated anodic charge as a function of Na₂SO₄ concentration, step at 3.0 V for 1 s. The charge for 0.1 M KClO₄ is subtracted.

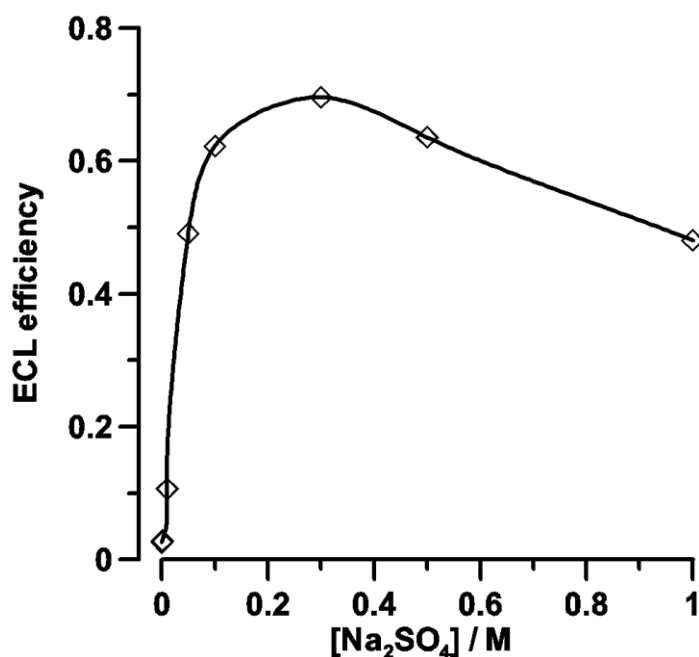


Figure S8. ECL efficiency as function of the SO₄²⁻ concentrations. The ECL efficiency is defined as photon emitted for amount of S₂O₈²⁻ generated. The integrated ECL intensity (from Figure 6 main text) at various Na₂SO₄ concentrations in 5 μM Ru(bpy)₃Cl₂ aqueous solutions; first step 3.0 V for 1 s, followed by a step to -2.0 V for 50 s. PMT bias 750 V.

Reference:

1. Yano, T.; Popa, E.; Tryk, D.A.; Hashimoto, K.; Fujishima, A. *J. Electrochem. Soc.* **1999**, *146* (3), 1081.
2. Yano, T.; Tryk, D.A.; Hashimoto, K.; Fujishima, A. *J. Electrochem. Soc.* **1998**, *145* (6), 1870