Supporting information

for

Electrogenerated Chemiluminescence of Luminol Mediated by Carbonate Electrochemical Oxidation at Boron-doped Diamond

Irkham,[1] Raishaqy R. Rais,[2] Tribidasari A. Ivandini,[2] Andrea Fiorani*[1] and Yasuaki Einaga*[1]

[1] Department of Chemistry, Keio University, 3-14-1 Hiyoshi, Yokohama 223−8522, Japan.

[2] Department of Chemistry, Faculty of Mathematics and Sciences, Universitas Indonesia, Kampus UI Depok, Jakarta 16-4424, Indonesia.

Table of Contents

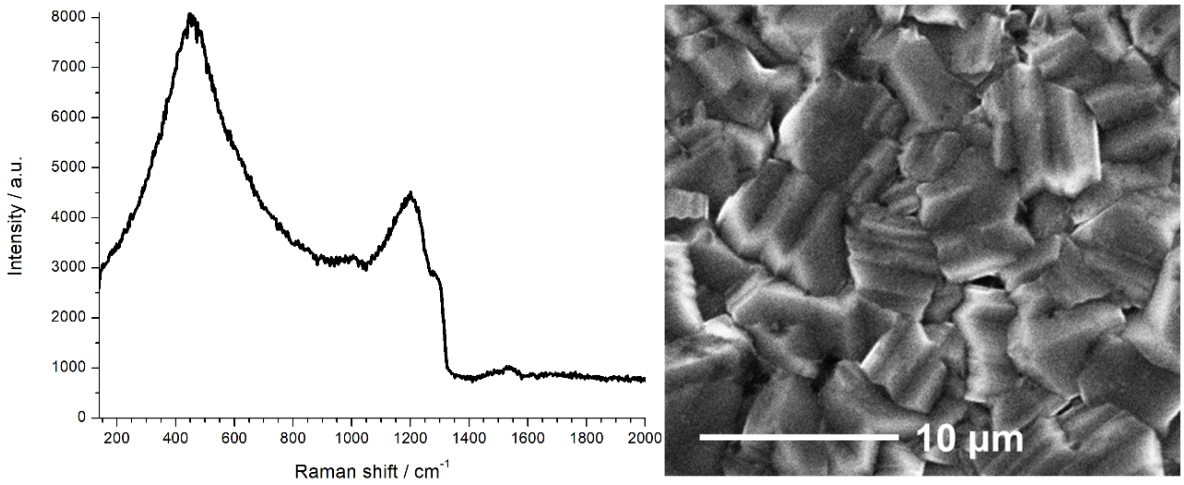

Figure S1. Raman spectrum (left) and SEM image (right) of 1% BDD used throughout all experiments.

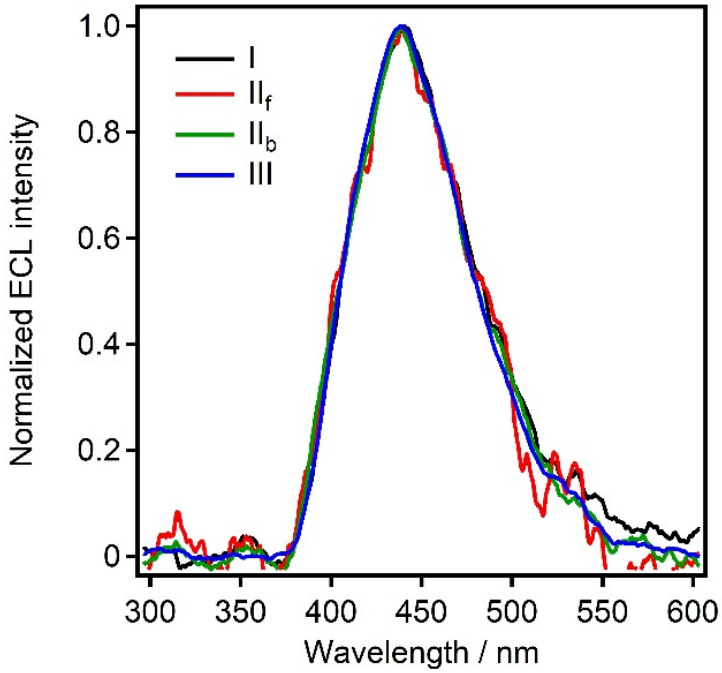

Figure S2. Normalized ECL spectra of 1 mM luminol in 500 mM of Na_2CO_3 obtained by CV at 100 mV s^{-1}. Spectra were acquired every 100 ms, and they are shown at selected potentials corresponding to the four peaks of Figure 1: I) 0.5 V, II_f) 3 V, II_b) 2 V, and III) 1.1 V.

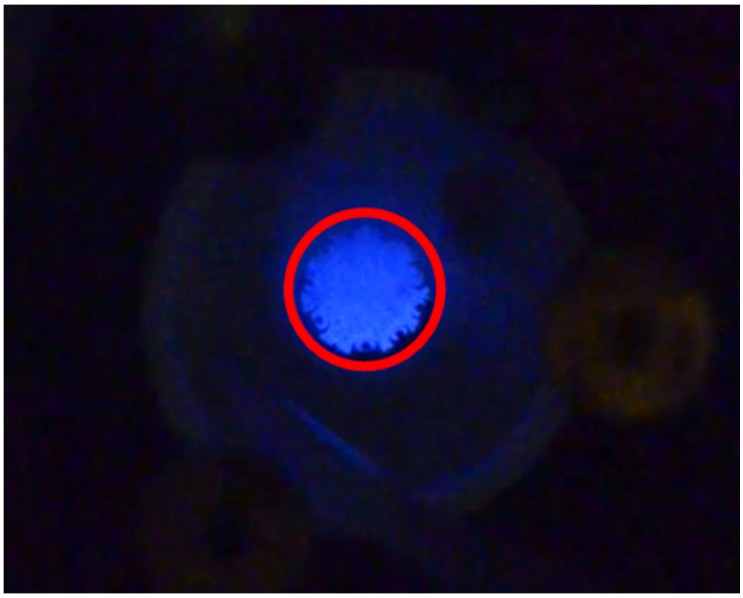

Figure S3. ECL image of 1 mM luminol in 500 mM of Na_2CO_3 at 3.5 V obtained during CV at 100 mV s^{-1}, from 0 V to 4 V, in the forward scan. The picture was taken from a video recording of the electrochemical cell, inside the dark box and using a camera DSLR Nikon D5100 with 50 mm fixed lens. The frame rate was 25 FPS. Oxygen bubbles from water oxidation are clearly visible at the edge of the electrode, giving it a jagged circumference. The actual electrode diameter is delimited by the red circle.

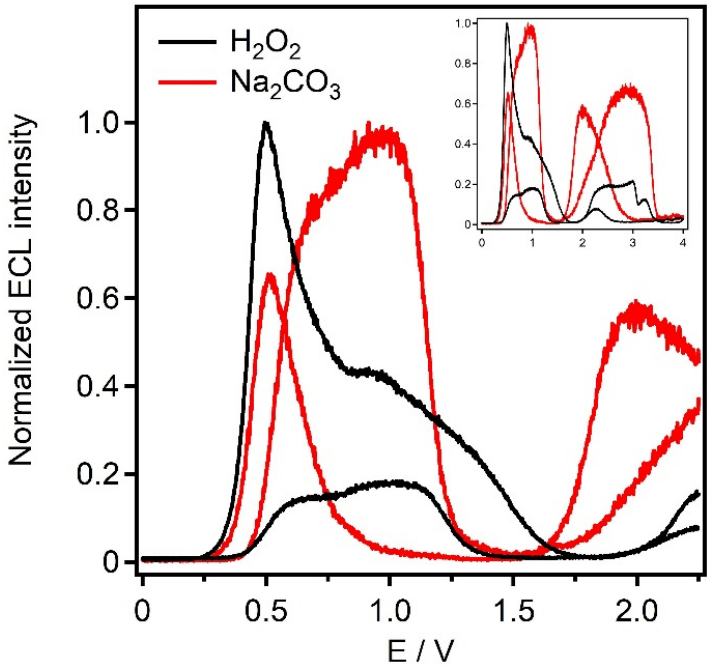

Figure S4. Comparison of ECL profile: 100 μM luminol in 200 mM phosphate buffer added with 10 mM H_2O_2 (black) and 100 μM luminol in 100 mM Na_2CO_3 (red) at pH 12. Scan rate, 100 mV s^{-1}. The ECL has been normalized for clarity to highlight the potential of both emissions.

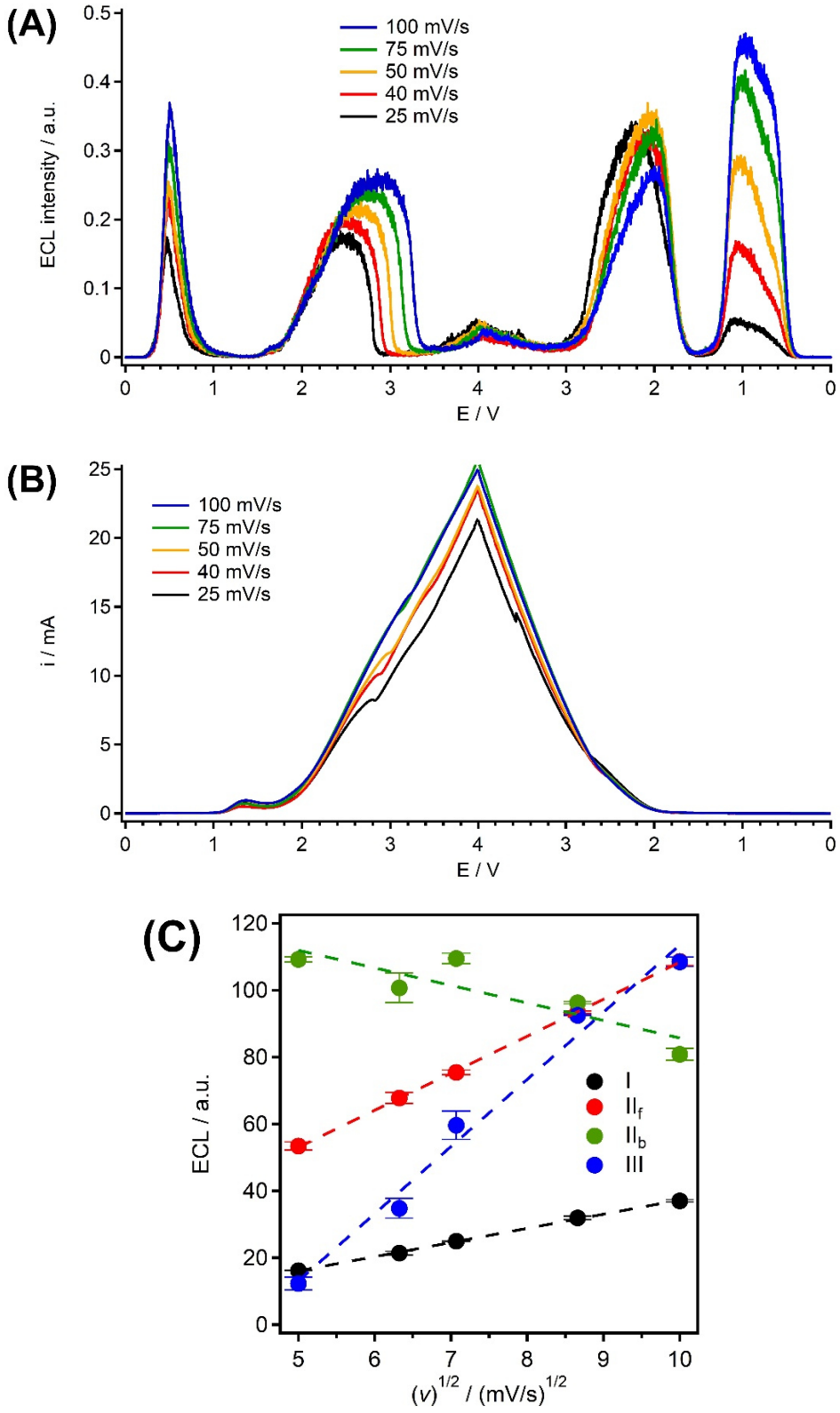

Figure S5. (A) ECL and (B) CV measurements with scan rate variation of 100 µM luminol in 100 mM Na_2CO_3 at pH 12. (C) Plot of the integrated ECL intensity as function of square root of the scan rate.

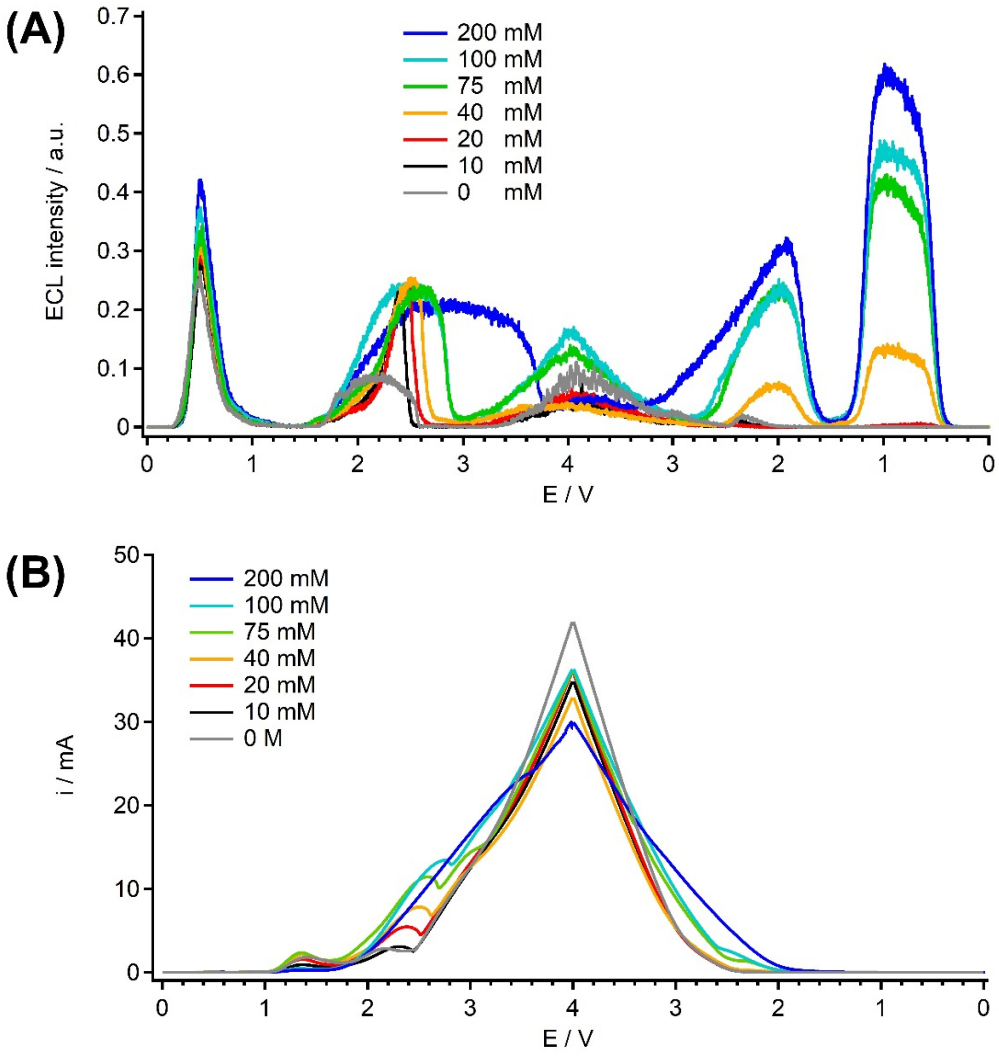

Figure S6. (A) ECL intensity and (B) CV measurements of 100 µM luminol in Na_2CO_3 at different concentrations (pH 12). The ionic strength was adjusted with the addition of $NaClO_4$. Scan rate, 100 mV s^{-1}.

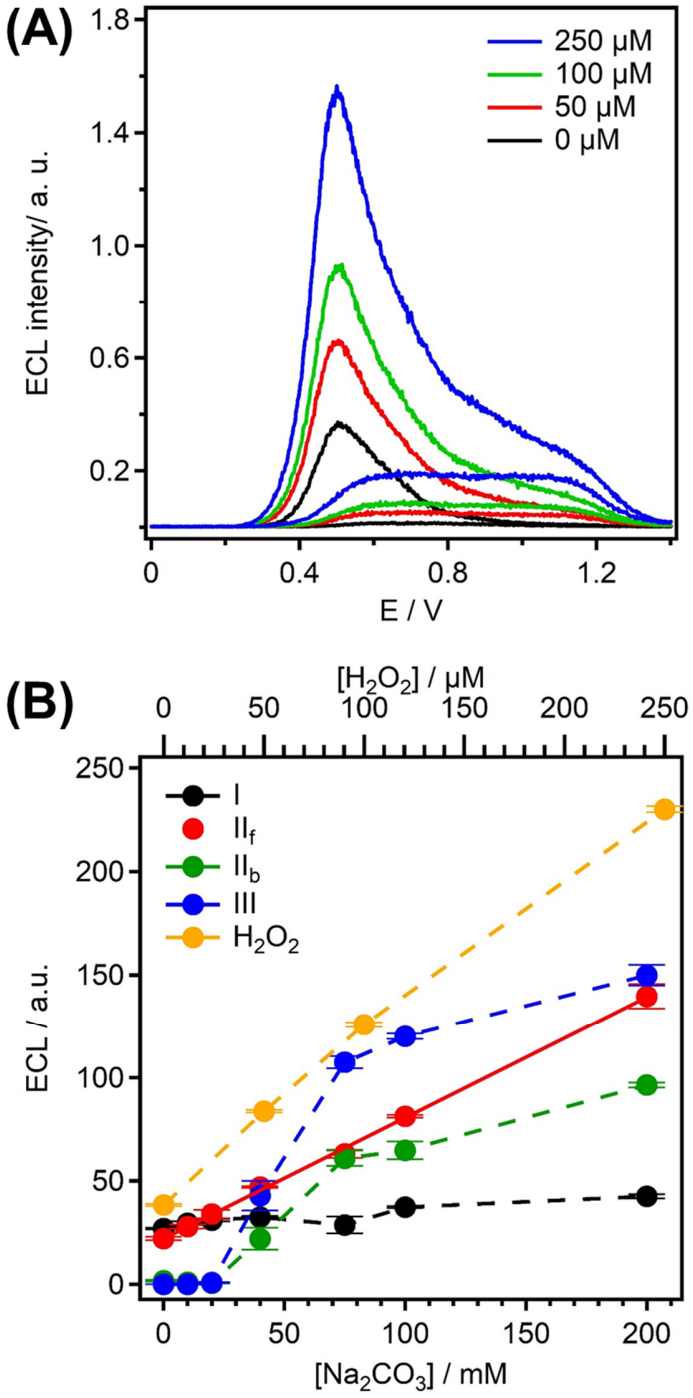

Figure S7. (A) ECL intensity of 100 μM luminol in 100 mM Na_2CO_3 (pH 12) with addition of 50 μM, 100 μM and 250 μM of H_2O_2. (B) Comparison of integrated ECL intensity between luminol/carbonate (Figure 2) and luminol/H_2O_2 (Figure S7A).

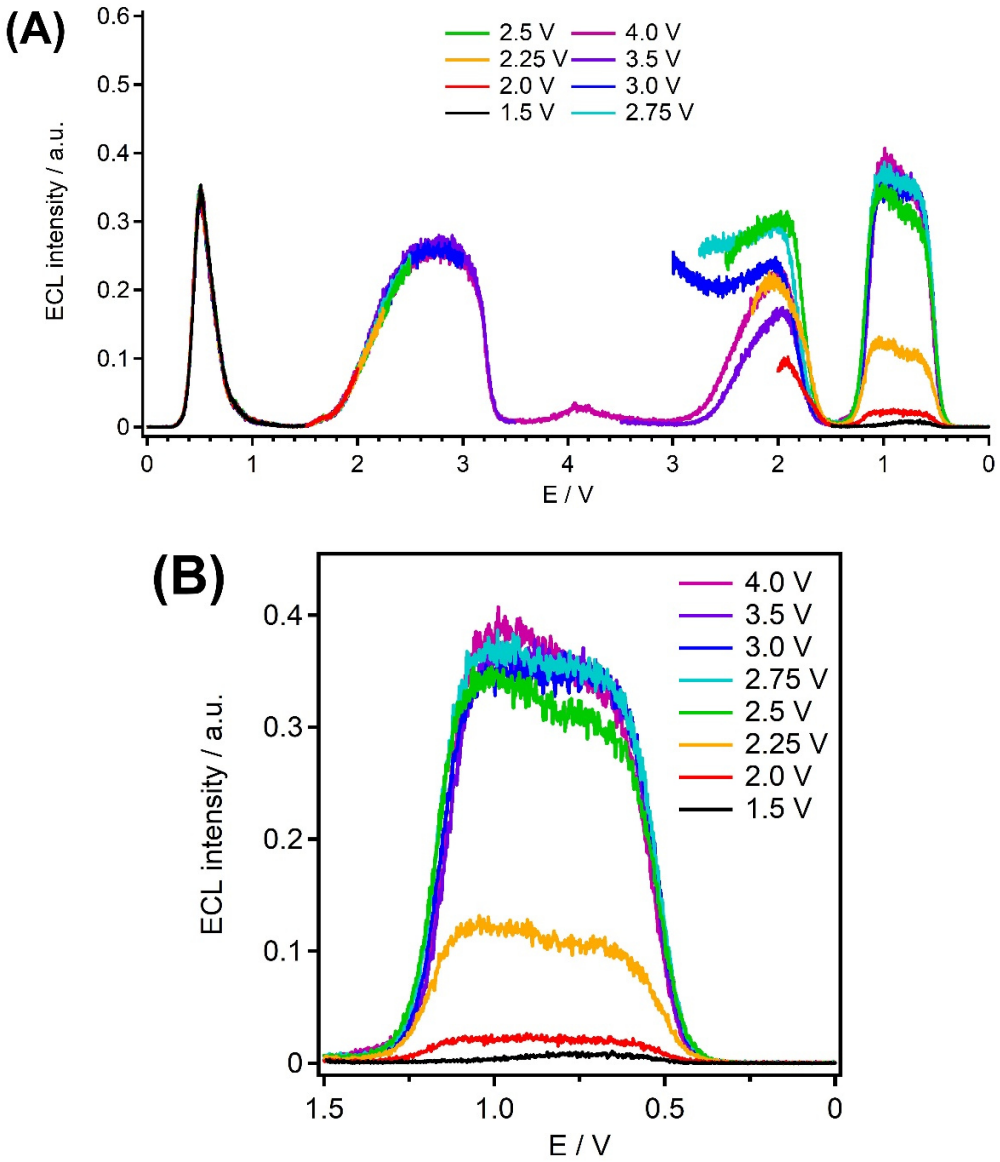

Figure S8. (A) CV-ECL measurement of 100 µM luminol in 100 mM Na_2CO_3 (pH 12) for different upper vertex potentials. (B) Detail of peak III. Scan rate, 100 mV s^{-1}. Reference electrode: Ag/AgCl (KCl sat).

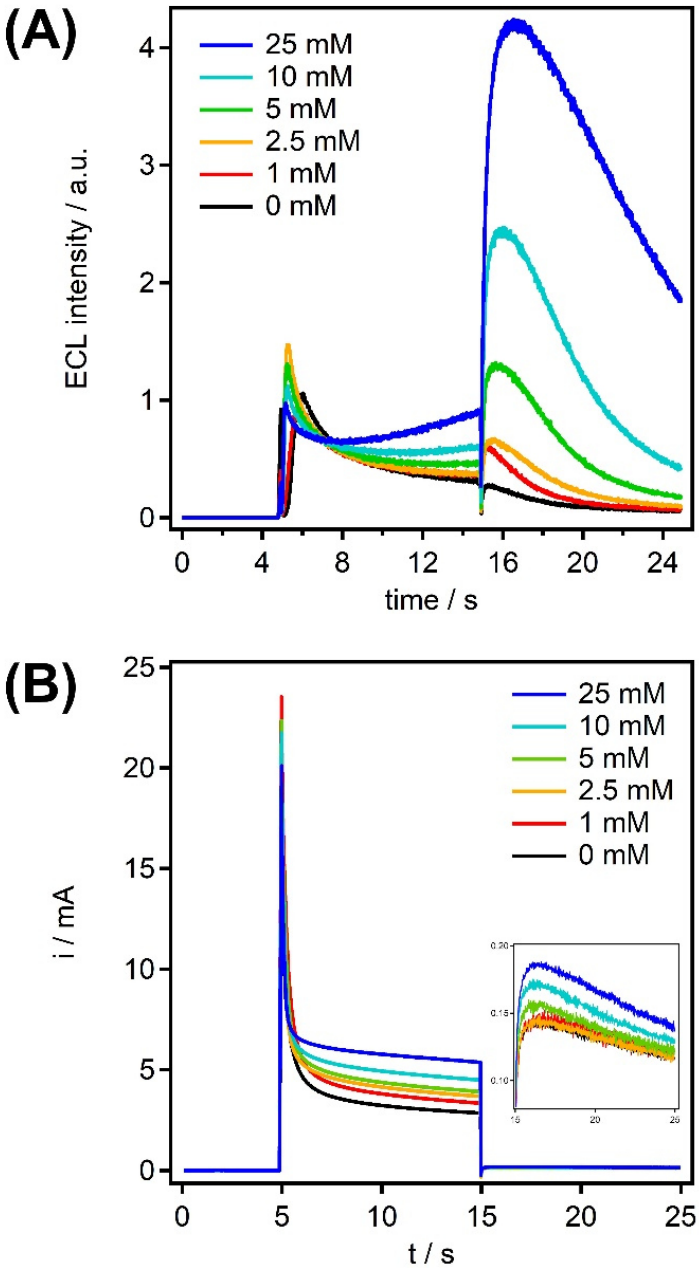

Figure S9. (A) ECL and (B) CA measurement of 1 mM luminol in different concentrations of Na_2CO_3. The three steps of the CA where: $E_1 = 0$ V, $t_1 = 5$ s; $E_2 = 2.5$ V, $t_2 = 10$ s; $E_3 = 1.1$ V, $t_3 = 10$ s. Reference electrode: Ag/AgCl (KCl sat).

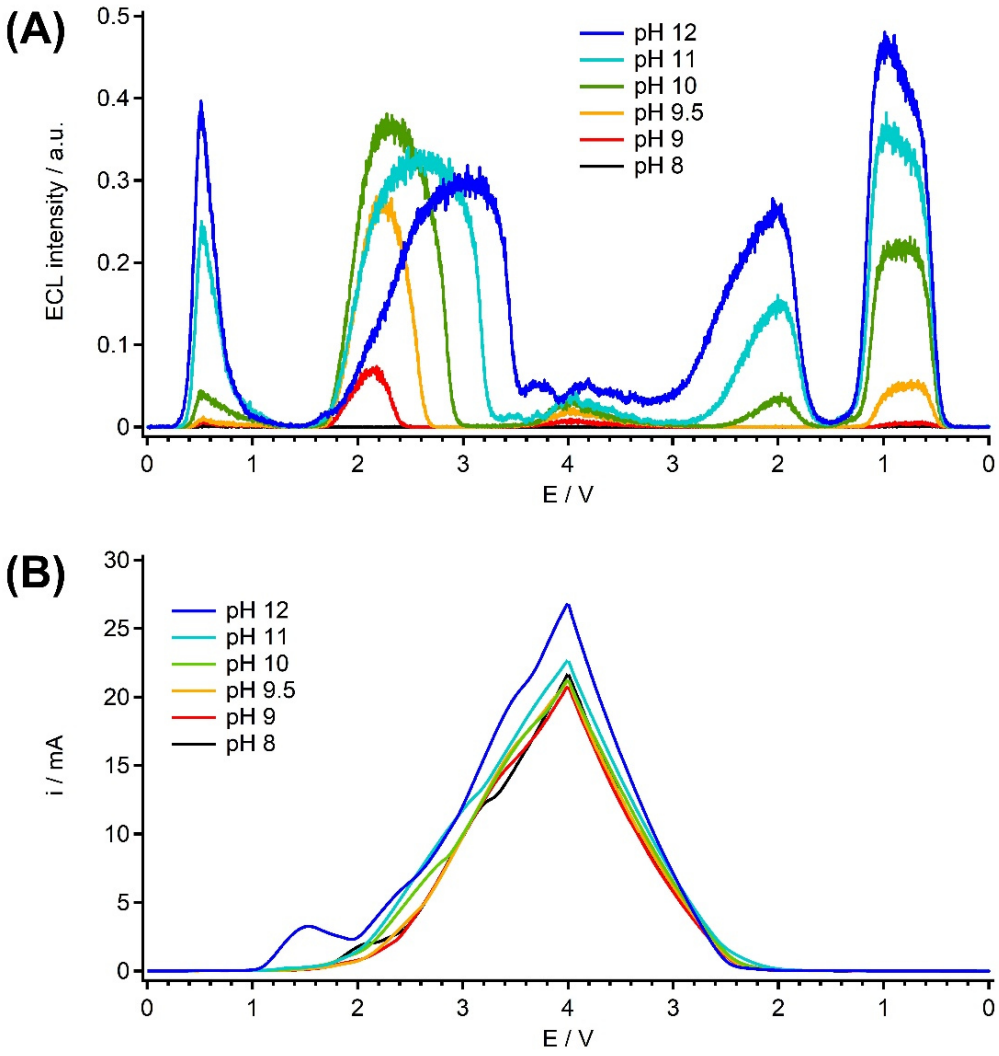

Figure S10. (A) ECL and (B) CV measurement of 100 µM luminol in 100 mM Na_2CO_3 at different pH. Scan rate, 100 mV s^{-1}. Reference electrode: Ag/AgCl (KCl sat).

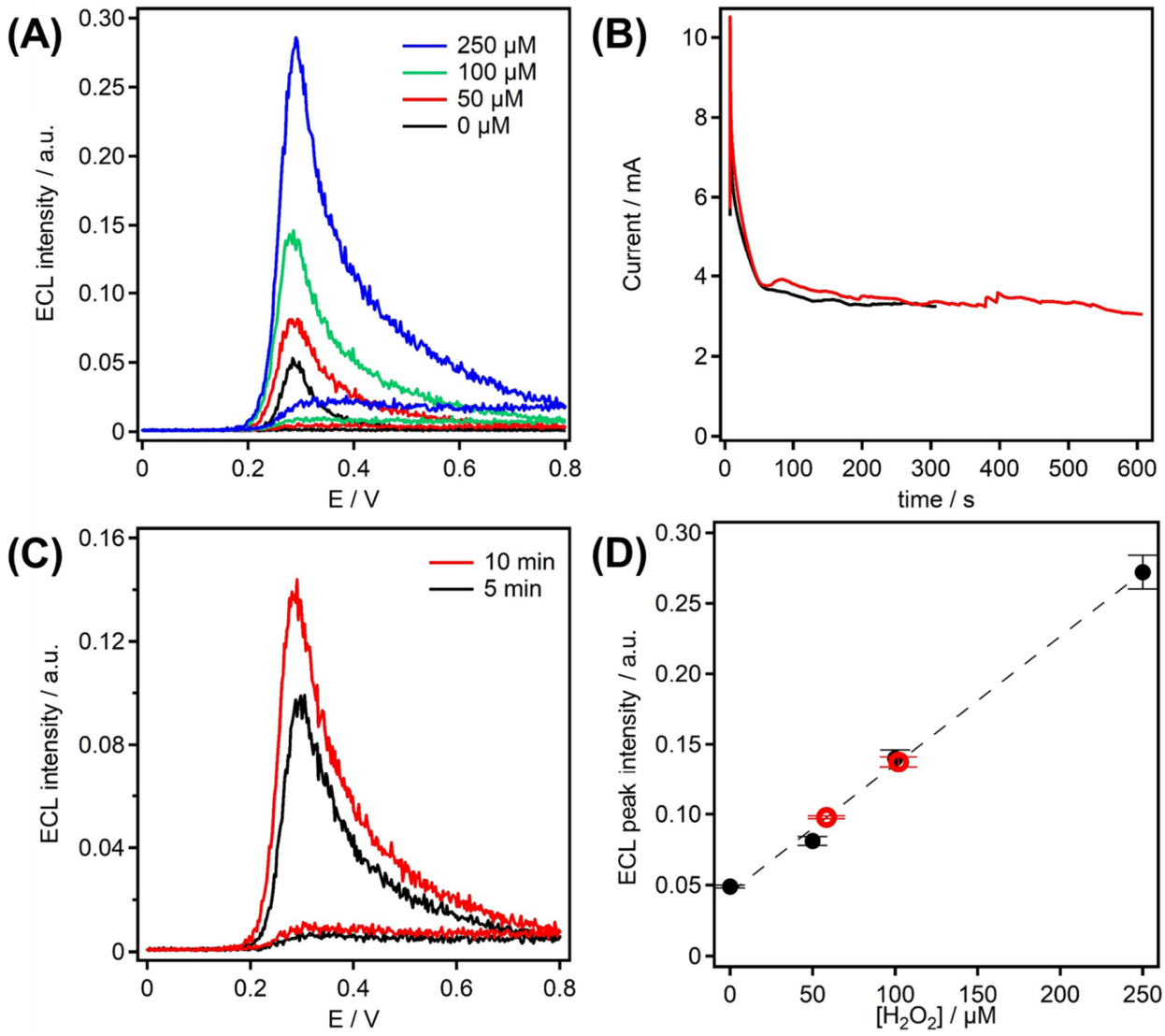

Figure S11. (A) ECL intensity for 50 µM luminol in 100 mM Na_2CO_3 (pH 12) with addition of 50 µM, 100 µM and 250 µM of H_2O_2. (B) Electrolysis of 100 mM Na_2CO_3 (3 ml) at 2.5 V for 5 min and 10 min. (C) ECL intensity of electrolyzed carbonate solution with 50 µM luminol. (D) Calibration curve for H_2O_2 concentration from (A) as function of the ECL peak intensity (black), and working curve (dashed line); concentration measured from carbonate electrolysis after 5 and 10 minutes (red). Reference electrode: Ag/AgCl (KCl sat).

The volume of Na_2CO_3 used in the electrolysis was 3 ml. After the electrolysis (Figure S11B), 2.5 ml were collected and added of luminol to obtain a final concentration of 50 μM in a final volume of 5 ml. This solution was analyzed by ECL (Figure S11C). The concentration of H_2O_2 in the electrolyzed carbonate solution was measured by using the working line (ECL peak intensity = $0.00091[H_2O_2] + 0.0445$, Figure S11D). The results of this quantification are summarized in Table S1.

Table S1. Data on the quantification of hydrogen peroxide from the carbonate electrolysis: 100 mM Na_2CO_3 at pH 12.

Electrolysis / min	$[H_2O_2]$ / μM	H_2O_2 / mol	Q / C	FE / %	Production rate / mol s^{-1} cm^{-2}
5	117	3.5×10^{-7}	1.1	6.2	1.8×10^{-9}
10	204	6.1×10^{-7}	2.1	5.5	1.6×10^{-9}