

Enhanced electrogenerated chemiluminescence of ruthenium tris(2,2')bipyridyl/triethylamine system on a boron-doped diamond nanograin array

**Yongtak Yang,^a Jeong-Wook Oh,^a Yang-Rae Kim,^a Chiaki Terashima,^b
Akira Fujishima,^c Jong Seung Kim^{*d} and Hasuck Kim^{*a}**

a Department of Chemistry, Seoul National University, Seoul 151-747, Korea. E-mail: hasuckim@snu.ac.kr;
Fax: +82-2-880-1568; Tel: +82-2-880-6666

b Technology Research and Development Department, General Technology Division, Central Japan Railway,
1545-33 Ohyama, Komaki City, Aichi 485-0801, Japan.

c Kanagawa Academy of Science and Technology, KSP, 3-2-1 Sakado, Kawasaki 213-0012, Japan.

d Department of Chemistry, Korea University, Seoul 136-701, Korea. E-mail: jongskim@korea.ac.kr

EXPERIMENTAL

Reagents and materials.

$\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (minimum purity 98%) and triethylamine (TEA) were obtained from Aldrich (Milwaukee, WI, USA) and used as received. TEA was dissolved in 0.1 M phosphate-buffered saline (PBS), and the pH of the resulting solution was adjusted to 7.4 with NaOH or NaH_2PO_4 . In the electrogenerated chemiluminescence (ECL) analysis of aqueous $\text{Ru}(\text{bpy})_3^{2+}$, the optimum pH of the TEA buffer solution is approximately 7-8, and a concentrated TEA (around 100 mM) is usually used to achieve high ECL intensity.¹ Other chemicals were of analytical grade and were used as received. Deionized double-distilled water was used to prepare all the solutions. The boron-doped diamond (BDD) electrode and BDD nanograin array were provided by Fujishima group.²

Electrochemistry studies and ECL measurements.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy were performed using a CH Instruments Model 660 electrochemical analyzer (Austin, TX, USA) equipped with a conventional three-electrode electrochemical cell. A working electrode (BDD electrode or BDD nanograss array), a platinum wire auxiliary electrode, and a Ag/AgCl (3 M KCl) reference electrode were used. The geometric surface area of the working electrode was 0.33 cm^2 . All potentials were measured versus the Ag/AgCl reference at room temperature. The electrochemical impedance spectra were obtained at an amplitude of 10 mV (rms) in the frequency range from 0.5 Hz to 100 kHz. The impedance data were fitted to an appropriate equivalent circuit by using Zsimpwin 3.0 software (Echem Software). The ECL intensity and the CV curves were measured using CHI 660 combined with a photomultiplier tube (PMT, Hamamatsu R7400U-20, H6780-20 photosensor module, 0.5 counts/s). The current density and ECL intensity (PMT output) were calculated from the geometric surface area of the electrodes.

References

- 1 J. K. Leland and M. J. Powell, *J. Electrochem. Soc.*, 1990, **137**, 3127-3131.
- 2 M. Wei, C. Terashima, M. Lv, A. Fujishima and Z. Z. Gu, *Chem. Commun.*, 2009, **24**, 3624-3626.

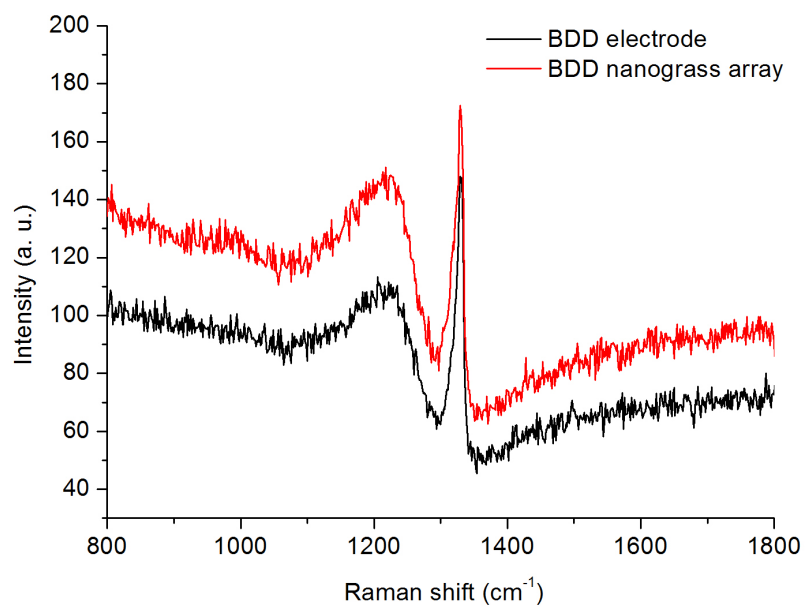


Figure S1. Raman spectra of the BDD electrode (black) and BDD nanoglass array (red).

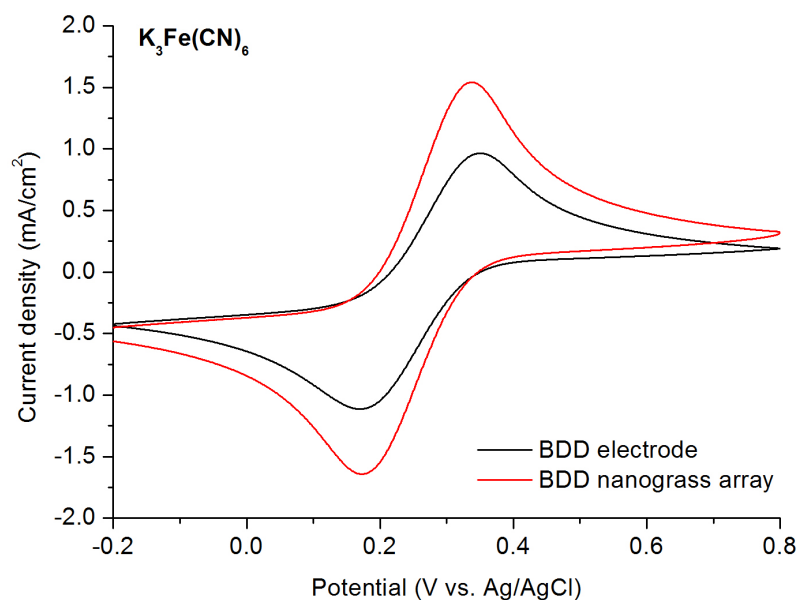


Figure S2. CV curves of 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ in 1 M KCl at the BDD electrode (black) and BDD nanograss array (red). The scan rate was 100 mV/s.

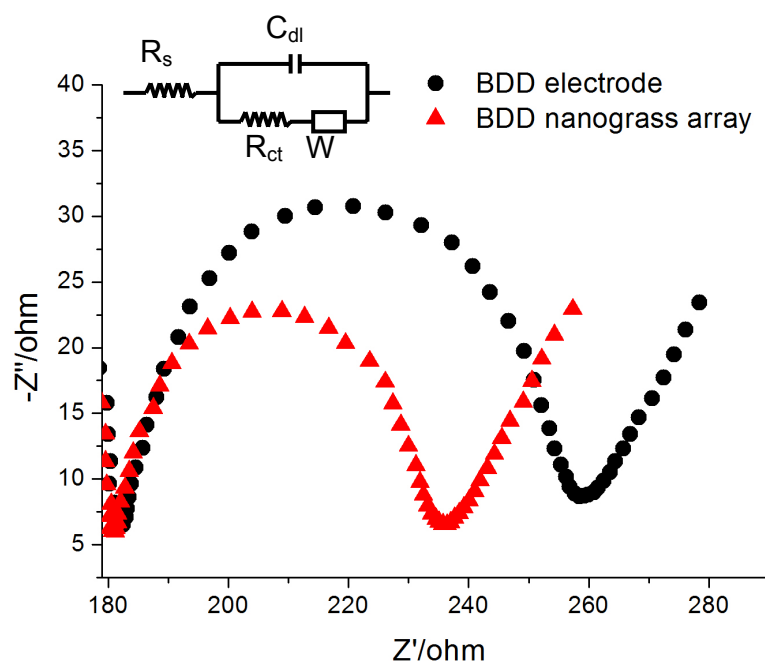


Figure S3. Nyquist plots of $10 \text{ mM Fe(CN)}_6^{3-/4-}$ in 0.1 M PBS obtained at the BDD electrode (black), and BDD nanoglass array (red). The frequency range was from 0.5 Hz to 100 kHz . The ac amplitude of 10 mV was applied.

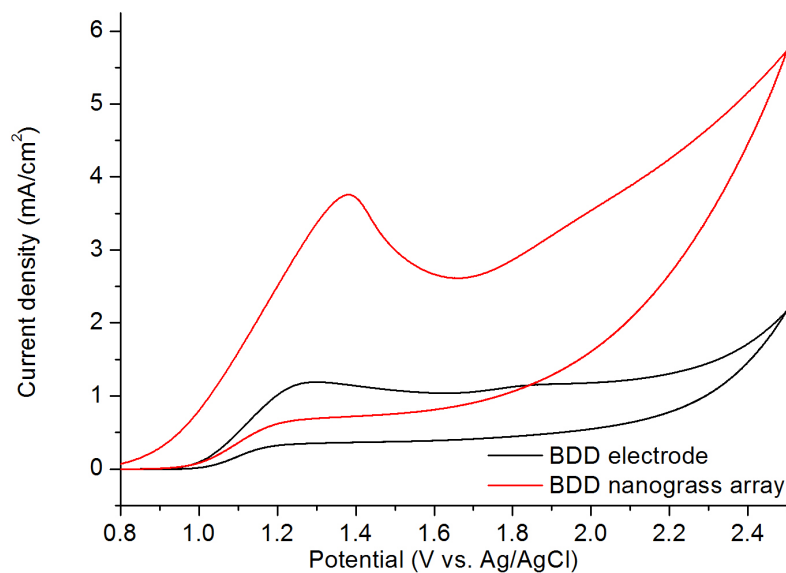


Figure S4. CV curves at the BDD electrode (black) and BDD nanoglass array (red) in 0.1 M PBS (pH 7.4) containing 100 μM $\text{Ru}(\text{bpy})_3^{2+}$ and 0.1 M TPA. The scan rate was 100 mV/s.