Electronic Supplementary Information (ESI)

High-yield fabrication of $Ti_3C_2T_x$ MXene Quantum Dots and their Electrochemiluminescence Behavior

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Content

Experimental Section

Chemical Reagents**:** Ti_3AlC_2 power (200 mesh) was bought from Beijing HWRK Chem Co., Ltd. ITO electrode (<10 ohm sq^{-1}) was bought from Zhuhai Kaivo Optoelectronic Technology Co., Ltd. 40% HF solution was bought from Shanghai Titan Scientific Co., Ltd. TPrA was obtained from the SIGMA-ALDRICH. 25% TMAOH solution, 30% H_2O_2 solution, NaOH, $K_2S_2O_8$, $NaH_2PO_4 \cdot 2H_2O$, $Na_2HPO_4 \cdot 12H_2O$, KCl was bought from Sinopharm Chemical Reagent Co. Ltd. All reagents were used without any further purification. Ultrapure water was used during the whole experiment period.

Characterization**:** Transmission electron microscopy (TEM) and High-resolution TEM (HRTEM) images were acquired on the FEI/Philips Tecnai F20 (200 kV) transmission electron microscope. Scanning Electron Microscopy (SEM) characterization was conducted on Carl Zeiss Supra 55 SEM (acceleration voltage 15 kV). XRD patterns were characterized by the PIXcel3D X-ray diffractometer (Empyrean, Holland Panalytical) equipped with Cu Kα radiation (λ=0.154178 nm). X-ray photoelectron spectra (XPS) were performed with a KRATOS Axis ultra DLD X-ray photoelectron spectrometer with monochromatised Al Kα X-rays (hν= 1283.3 eV). Fourier transform Infrared (FT-IR) spectra were recorded on a FT-IR spectrometer (Spectrum One, PerkinElmer) applying KBr tablet method. Raman spectra were obtained on a customized LabRAM HR800 confocal Raman microscope (Horiba Jobin Yvon, incidence laser 532 nm). UV-vis absorption spectra were obtained with a JASCO J-815 spectropolarimeter. Photoluminescence (PL) and PL excitation (PLE) spectra were measured on a Horiba Jobin Yvon (FluoroMax 4) luminescence spectrometer.

***Synthesis of MQDs*:** First of all, MXene was prepared from parent MAX by HF etching according to tutorials previously reported. Briefly, 0.5 g Ti_3AlC_2 was added slowly in 10 mL 40% HF acid in 5 minutes course (Caution: HF acid must be carefully treated with plastic beaker in a fuming hood and be avoided from touching by skin or sucked through breathing!). The mixture was stirred for 5 h to fully etch the Al layer selectively in Ti_3AlC_2. After that, 50 mL ultrapure water was added to dilute and end the etching, then the $Ti_3C_2T_x$ turbid fluid was centrifuged (3500 rpm) and washed several times until the pH was near neutral. Subsequently, vacuum filtration was conducted to wash the $Ti_3C_2T_x$ particles totally, and the $Ti_3C_2T_x$ powder was obtained by vacuum drying at 80 °C overnight for further use. To prepare TMAOH-intercalated $Ti_3C_2T_x$, 0.1 g $Ti_3C_2T_x$ powder was added into 10 mL 1% TMAOH solution stirring for 12 h. After that, centrifugation (8000 rpm), vacuum filtration and vacuum drying was carried out sequentially to get TMAOH-intercalated $Ti_3C_2T_x$ powder for further use. Finally, to produce MQDs with appreciable output, 50 mg TMAOH-intercalated $Ti_3C_2T_x$ powder was added into 10 mL 2.5% TMAOH solution, then the mixture was refluxed at 110 °C for one day. After that, centrifugation (12000 rpm) was adopted to remove the larger $Ti_3C_2T_x$ particles, and the supernatant was further placed in a 200 °C vacuum drying oven overnight to remove the TMAOH and get pure MQDs powder. The throughput of QMDs was calculated to be ~60%.

***ECL Setup*:** All electrochemical (EC) and ECL measurement was conducted on a SECM-ECL multifunctional apparatus developed by our group (DyneChem Lt. Co., Changchun, China) as previously reported. We applied a three-electrode system to carry on the experiment, including ITO electrode as working electrode (WE), Ag/AgCl electrode in saturated KCl as reference electrode (RE), and Pt wire as counter electrode (CE). ITO electrode was ultrasonically cleaned in acetone, ethanol, and water for 10 minutes successively before each experiment. All supporting electrolyte solution was 0.1 M PBS (pH=7) containing 0.1 M KCl. For whole experiment, ECL luminophore MQDs was 0.1 mg mL^{-1}, and all coreactants was 50 mM, including TPrA, $Na_2C_2O_4$, $K_2S_2O_8$, H_2O_2. The electrolyte solution prepared was bubble with N_2 to remove the dissolved oxygen before each ECL test. All electrolyte solutions mixed with TPrA was ultrasonicated 20 min before ECL test to enhance the solubility of TPrA.

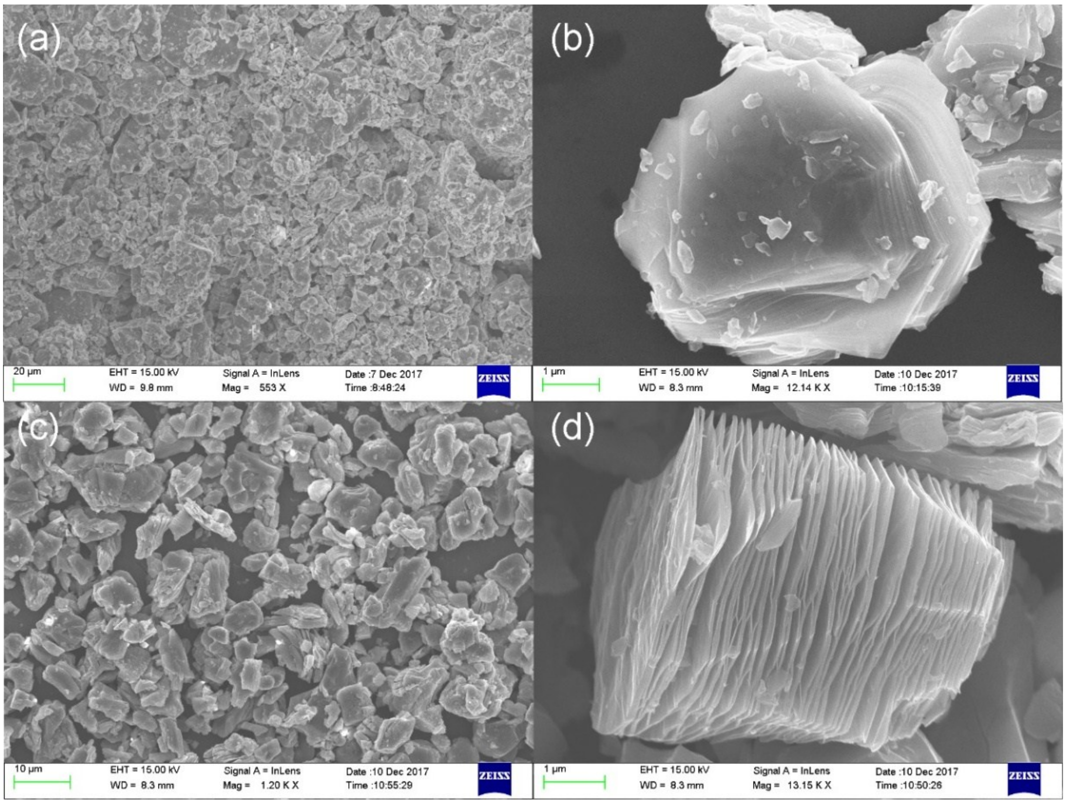

Fig. S1 (a) Low magnification SEM image of Ti_3AlC_2 particles. (b) High magnification SEM image of a single Ti_3AlC_2 particle. (c) Low magnification SEM image of $Ti_3C_2T_x$ particles. (d) High magnification SEM image of a single $Ti_3C_2T_x$ particle.

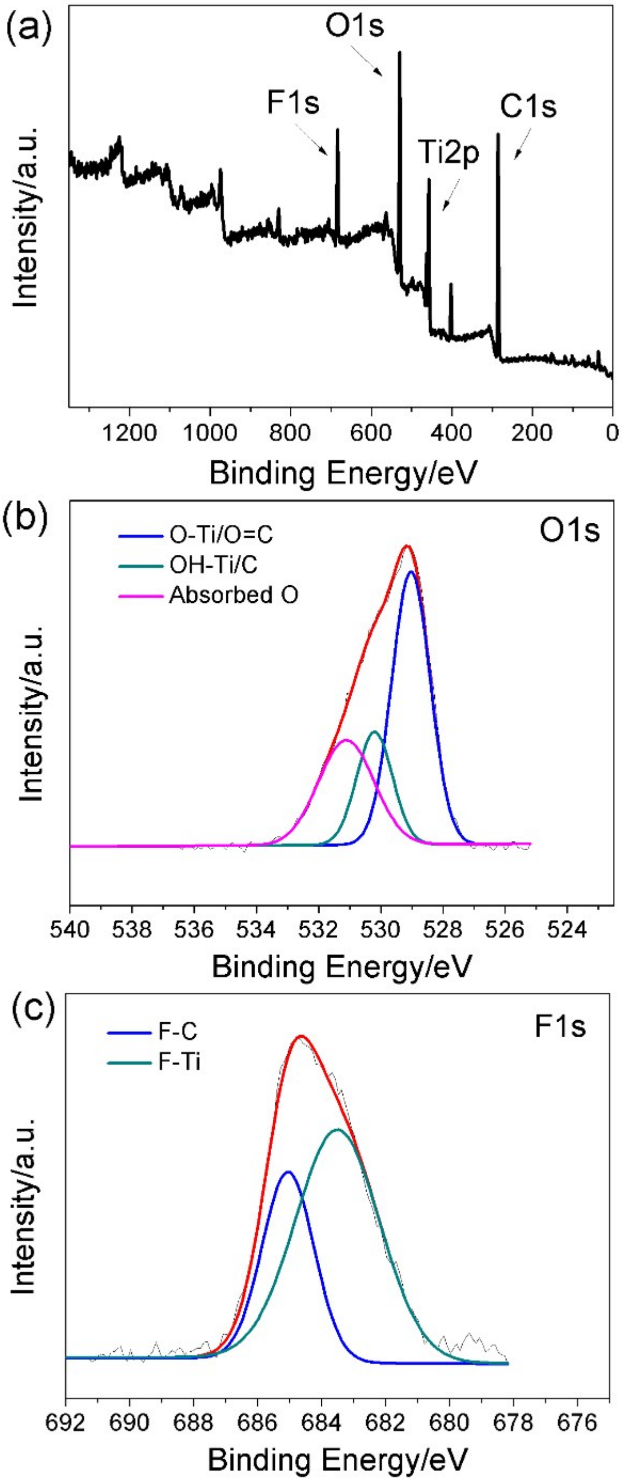

Fig. S2 (a) XPS survey spectrum of MQDs. (b) O 1s High-reslution XPS spectrum of MQDs. (c) F 1s High-reslution XPS spectrum of MQDs.

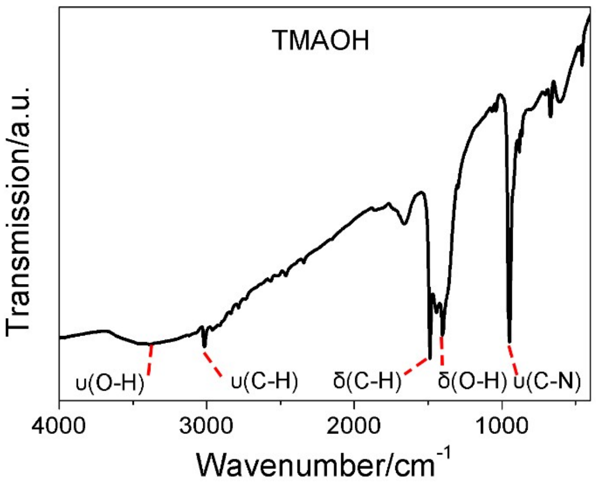

Fig. S3 FT-IR spectrum of TAMOH.

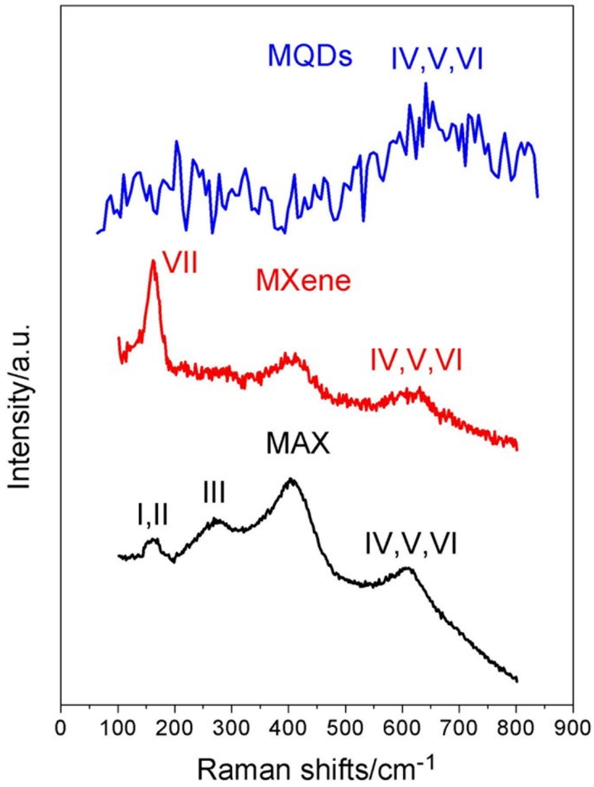

Fig. S4 Raman spectra of MAX, MXene, and MQDs.

Raman spectra of Ti_3AlC_2 MAX, $Ti_3C_2T_x$ MXene and $Ti_3C_2T_x$ MQDs were shown in Fig. S4. As for MAX, Raman spectrum could be found similarity with results previously reported by Yury Gogotsi's group.[1] Peaks I, II and III at lower Raman shifts could be assigned to Al-Ti vibrations, while IV, V, and VI region at ~600 cm^{-1} probably belongs to Ti-C bonding. After etched by HF, peaks I~III vanished obviously and peaks IV~VI broadened and weakened, which suggested the removal of Al from the structure and formation of MXene. Besides, a sharp and strong peak VII was observed for MXene, which should belong to Ti-O bonding formed during etching process.[2] With regard to MQDs, Raman spectrum became more broad and weak, which perhaps ascribed to the somewhat amorphous state of MQDs. Notwithstanding, Ti-C bonding could be recognized at the less obvious rise labeled "IV,V,VI".[3] All in all, Raman spectra as an effective tool interpreted the fabrication process (from MAX to MQDs), as well as revealed the Ti-C bonding of MQDs, which also showed up in FT-IR spectrum (Fig. 1f).

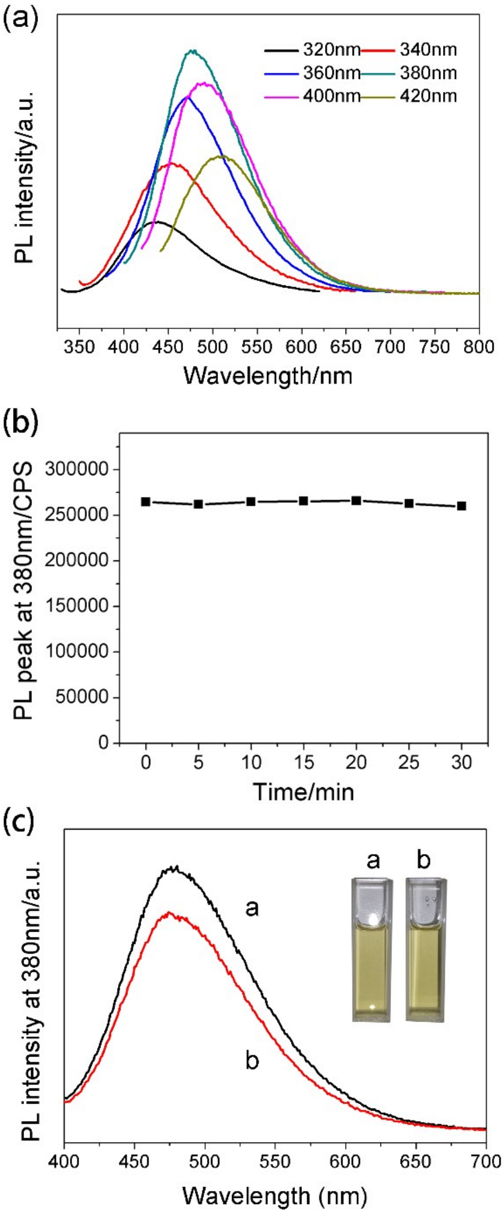

Fig. S5 (a) Excitation-dependent PL emission spectra of MQDs. (b) Anti-photobleaching performance of MQDs in 30 minutes. (c) Stability of MQDs. Image a and b are the image of initial MQDs solution and image of MQDs solution stored in ambient air for 10 days. Besides, curve a and b are corresponding PL emission spectra (λ_{ex}=380 nm) of MQDs solution.

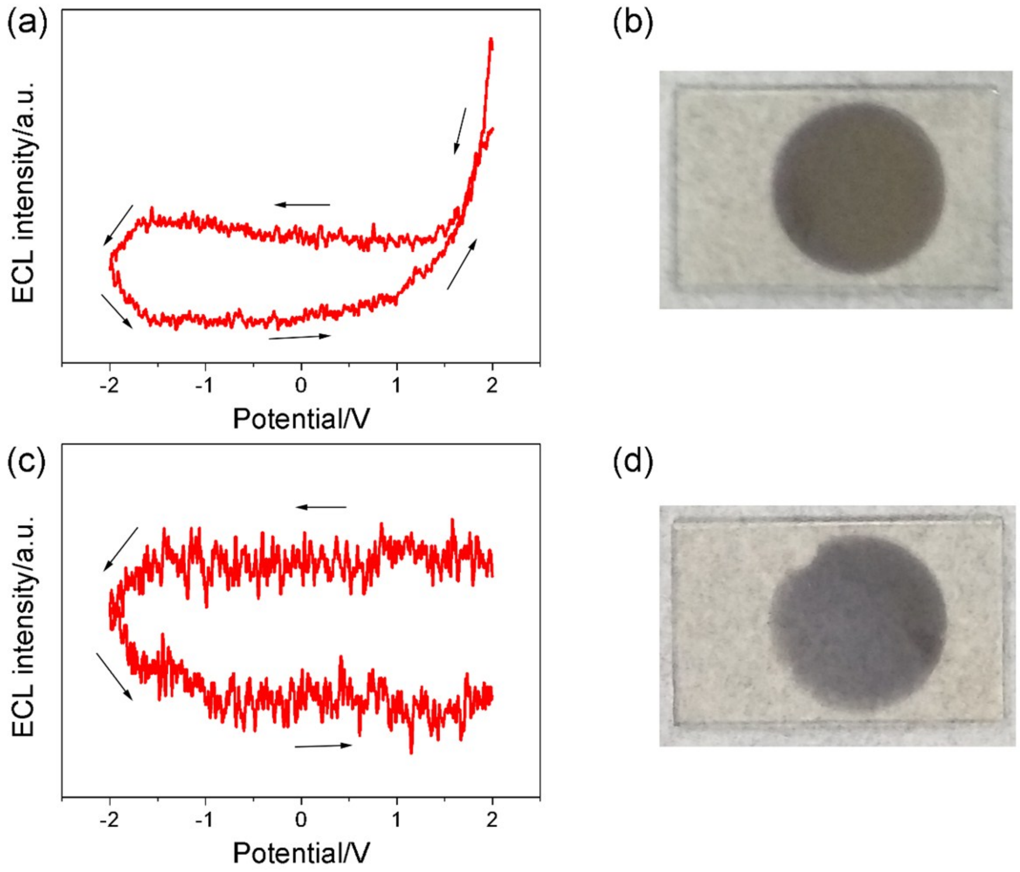

Fig. S6 (a, b) ECL signals with 0.1 mg mL^{-1} MQDs in 0.1 M PBS (pH=7) containing 0.1 M KCl scanned between -2 V and +2 V. Scan rate: 0.1 V s^{-1}. Optical image of ITO electrode scanned for 10 cycles. (c, d) Blank ECL signals in 0.1 M PBS (pH=7) containing 0.1 M KCl scanned between -2 V and +2 V. Scan rate: 0.1 V s^{-1}. Optical image of ITO electrode scanned for 10 cycles.

With this kind of ECL setup, the potential window couldn't be more negative than -1.5 V. As shown in Fig. S6a, abnormal ECL signal curve was observed on an ITO electrode when scanned from -2 V to +2 V. ECL signal was detected at the anode region while photocurrent value continued to decrease at the cathode region between -1.5 V and -2V. Besides, the ITO electrode transformed into a light black color (Fig. S6b) inducing the loss of photocurrent signals, which probably resulted from variation of ITO electrode or attribute to the cathode deposition of MQDs. Comparison experiment was conducted to find out the reason. Without MQDs, the blank ECL signals was shown in Fig. S6c, in which anode ECL signals disappeared while the decrease of photocurrent signals was similar with that of solution with MQDs. Besides, the ITO electrode after scanning 10 cycles became light black likewise (Fig. S6d). All these results suggested that applying ITO electrode in the ECL setup, the potential window during ECL tests should be configured as scan range from -1.5 V to +2 V to prevent the reduction of ITO electrode.

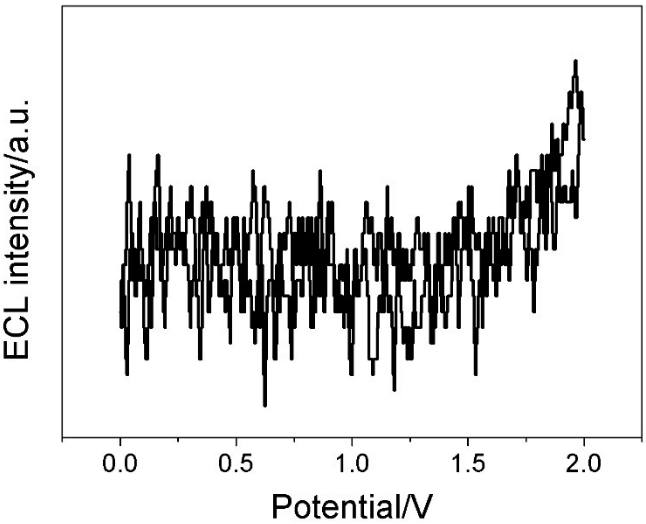

Fig. S7 Enlarged anode ECL response of 0.1 mg mL^{-1} MQDs in 0.1 M PBS (pH=7) containing 0.1 M KCl.

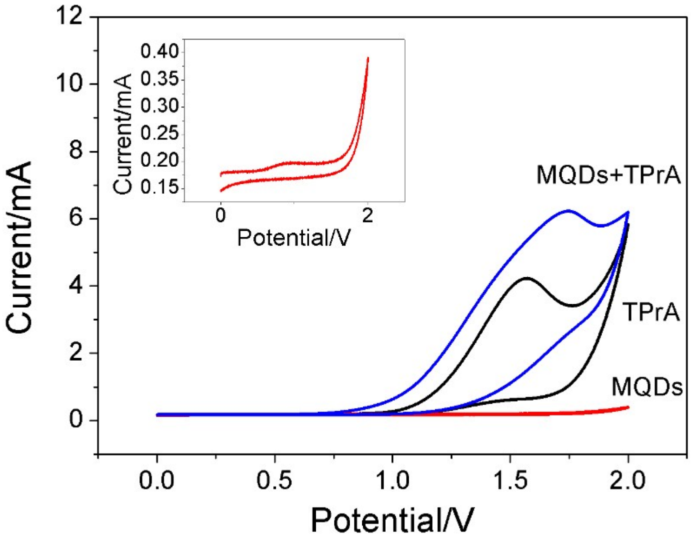

Fig. S8 CV curves (blue line) with both 0.1 mg mL^{-1} MQDs and 50 mM TPrA, (black line) with single 50 mM TPrA, and (red line) with only 0.1 mg mL^{-1} MQDs in 0.1 M PBS (pH=7) containing 0.1 M KCl. Inset is the enlarged CV curve of red line.

Table S1. Enhancement factors of the four conventional coreactants

ECL pathway	coreactant	Enhancement factors
Anode	TPrA	29-fold [a]
Anode	$Na_2C_2O_4$	2.7-fold [a]
Cathode	H_2O_2	*
Cathode	$K_2S_2O_8$	1.3-fold [b]

Note:

[a]: The ECL signals were about 29-fold or 2.7-fold higher than sole MQDs anode ECL signal;

[b]: The ECL signal was about 1.3-fold higher than background ($K_2S_2O_8$) signal.[4]

*: The ECL signal enhancement couldn't be defined.

All coreactants was 50 mM in ECL solution without further optimization.

Reference

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