Electronic Supplementary Information

Online chemiluminescence determination of hydroxyl radical using coumarin as probe

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Optimization of the concentrations of detection reagents.

Solution contained 200 μM COU, 100 μM H_2O_2 and 5 μM $FeCl_2$ were continuously stirred for 1h, then methanol (5%) were added to quench the reaction. This reaction solution was used as test solution to optimize the F-OCL detection conditions. Concentrations of NaOH from 0.5 to 3.0 mol L^{-1}, H_2O_2 from 0 to 0.8 mol L^{-1}, PMS from 0 to 0.4 mol L^{-1} were used to obtain optimized concentrations for F-OCL detection. The results were presented in Fig. S3.

Production of ·OH by TiO_2 photocatalysis.

Commercial grade TiO_2 (Aeroxide P25, 80% anatase and 20% rutile) was used in this study. A certain amount of P25 was added into glass beaker with 500 mL 200 μM COU solution to prepare P25-COU suspension with TiO_2 mass concentrations at 1, 10, 25 mg L^{-1}, respectively. The irradiation experiments were provided by a 300 W xenon lamp, and an AM 1.5 filter was used to best match the total solar spectrum. During photochemical experiment, the P25-COU suspension was put under the xenon lamp with distance about 15 cm and the suspension was constantly stirred. In-situ soil solution sampler was put into P25- COU suspension to collect analytical solution online by a peristaltic pump, and the solution was online detected by using flow oxidization CL method. On the other hand, 5 mL of suspension was collected at given time intervals, and 0.5 mL methanol was added to quench ·OH, then the suspension was centrifuged and filtered through pre-rinsed 0.22 μm Nylon membranes. The filtered supernatants were analyzed by HPLC combined with fluorescence detection and F-OCL method.

Verification of stability and repeatability of the F-OCL method.

COU/·OH reaction solution produced by TiO_2 photocatalysis was collected and kept at 4 °C in the dark. The CL signal of this solution was detected at different days to test the stability and repeatability of the method. The results were presented in Fig. S4.

Effect of some coexistent substances on the detection of ·OH by F-OCL method.

In order to study the possible matrix interference, some organic and inorganic substances with concentration of 1mM were mixed with COU (200 μM) and detected using the optimized F-OCL method, e.g., $FeCl_3$, $FeCl_2$, $MnCl_2$, $CaCl_2$, KCl, NaCl, $MgCl_2$, Na_2SO_4, $NaNO_3$, citric acid (CA), oxalic acid (OA), glucose (Glu) and L-histidine(L-his), etc. The results were presented in Fig. S5.

Detection of 7-hydroxycoumarin by high performance liquid chromatography.

Coumarin and monohydroxy coumarins in samples were detected by HPLC combined with fluorescence detection (Agilent 1200). An Agilent SB-C18 Zorbax column (5 μm, 4.6 × 150 mm) was used for the separation. The mobile phase was methanol/water (V/V = 45/65) and the flow rate was 1 mL min^{-1}. Fluorescence detector with excitation/emission wavelengths at 350/460 nm was used to detect 7OHC.[1] According to previous literatures, 6.1 % was of total ·OH radicals can be captured as 7OHC, therefore the total amount of ·OH was estimated as [7OHC]/6.1%.[2, 3]

Table S1 Chemical characteristics of soil samples

sample	pH	TOC (%)	DOC (mg/kg)	Fe (g/kg)	Al (g/kg)	Mn (mg/kg)	Cation Exchange Capacty (cmol/kg)
soil1	4.45	0.37	48.52	26.53	29.44	422	14.6
soil2	4.74	0.54	89.55	68.91	63.06	218	13.0
soil3	4.82	1.11	153.35	58.17	46.37	175	20.3
soil4	7.86	2.13	155.01	25.10	23.55	328	27.8

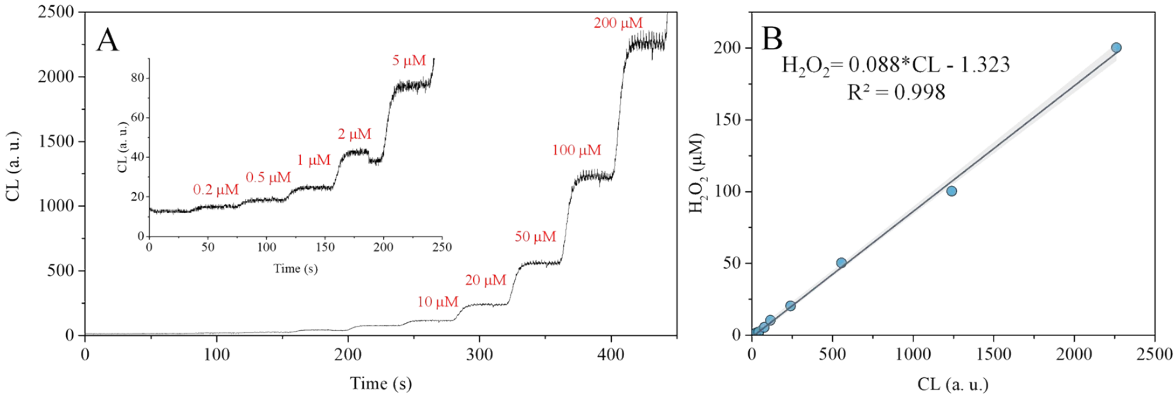

Fig. S1 (A) Detected CL signals of H_2O_2 with concentration ranges from 0 to 200 μM by AE based CL analysis. (B) the relationship between CL signal and the concentration of H_2O_2 (n = 3).

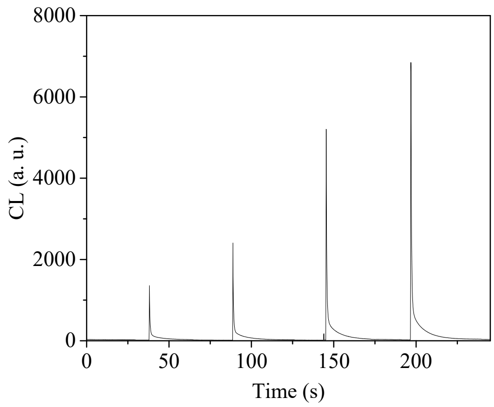

Fig. S2 Chemiluminescence signal of COU/·OH injected into PMS-H_2O_2-NaOH mixed solution.

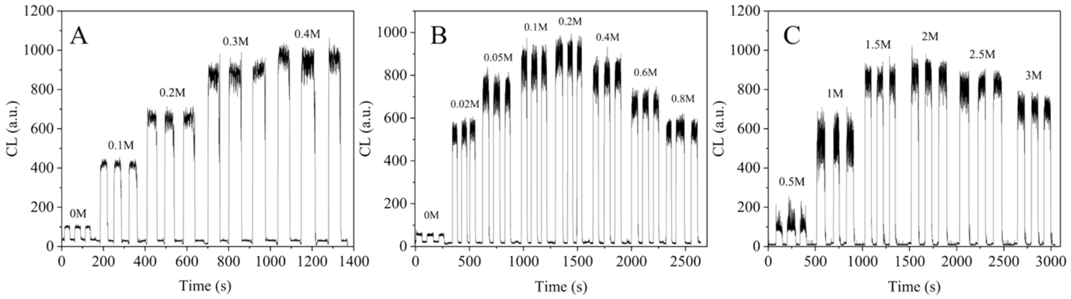

Fig. S3 Optimization of the CL detection conditions, including (A) PMS concentrations, (B) the concentration of H_2O_2, (C) the concentration of NaOH.

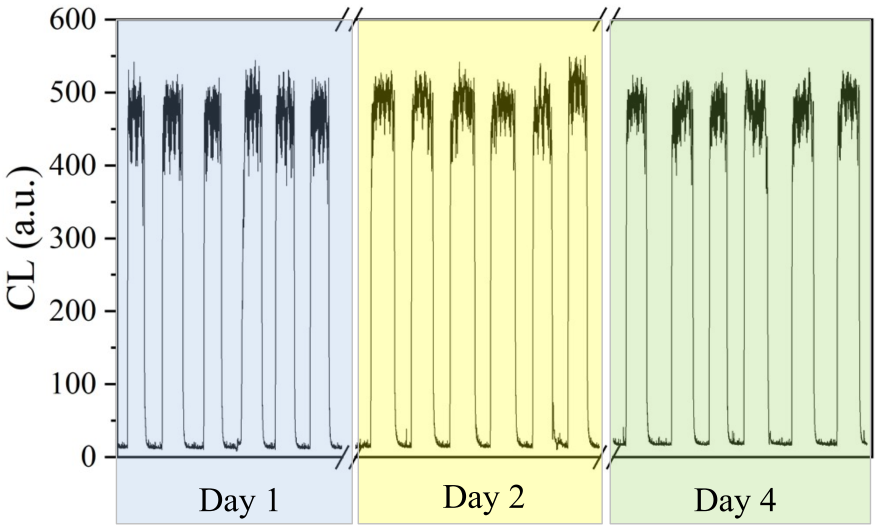

Fig.S4 CL signals of the same solution at different days.

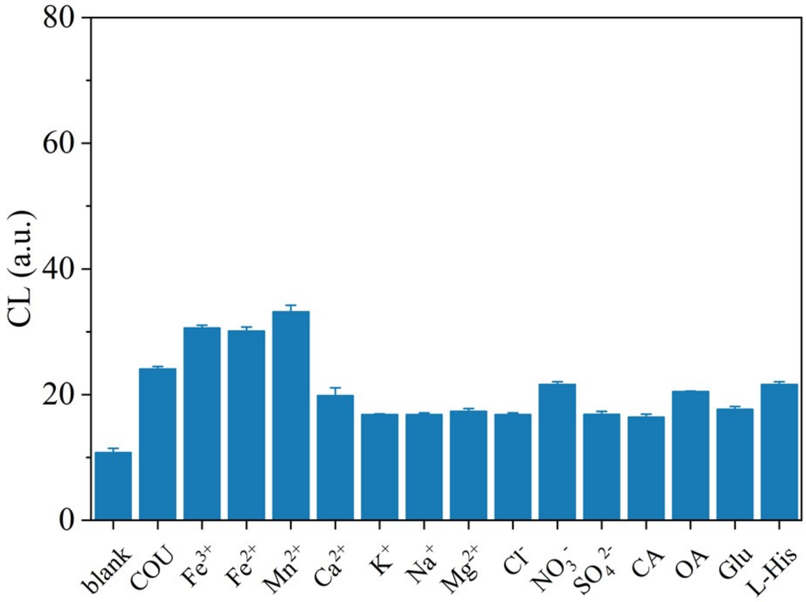

Fig. S5 CL signals of mixture solution containing 1 mM coexistent substances and 200 μM COU.

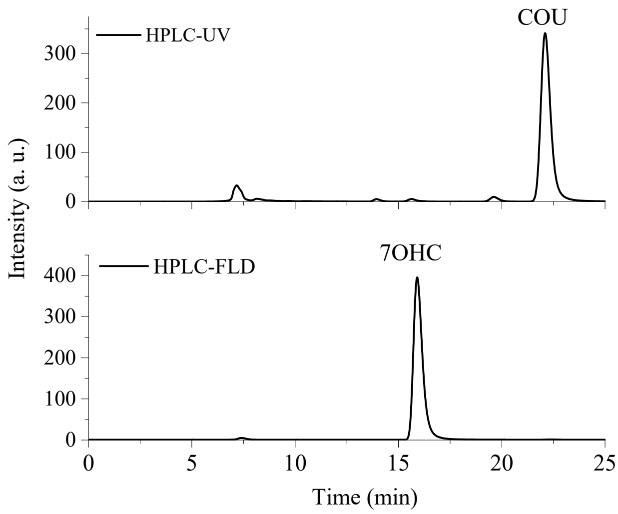

Fig. S6 Typical spectrogram of HPLC analysis.

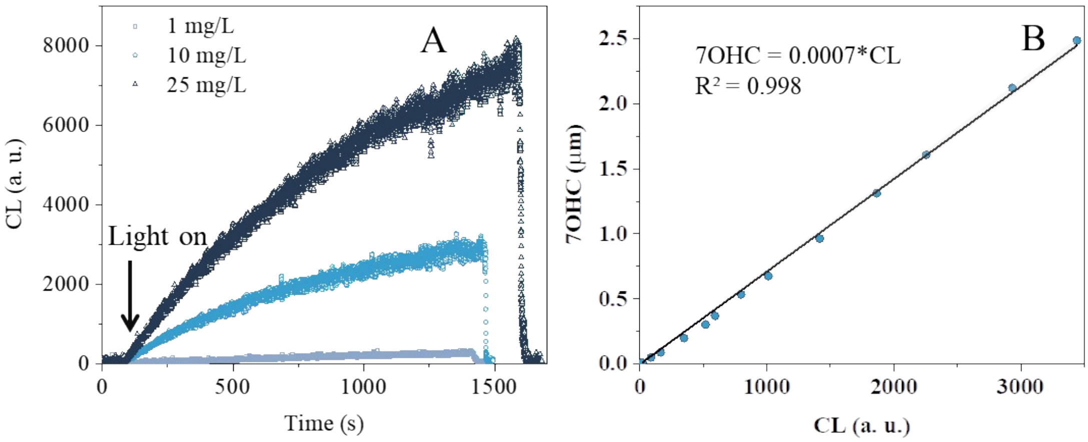

Fig. S7 (A) Dynamic changes of CL signal produced by the irradiation of TiO_2 suspensions (1, 10, 25 mg L^{-1}) detected by oxidization CL system, (B) the relationship between CL signal and the production of 7OHC detected by HPLC combined with fluorescence detection (n = 3).

References

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