Lucigenin/Co(tryptophan)$_2$ complex bifunctionalized graphene oxide: facile synthesis and unique chemiluminescence

Supporting information

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S1. CL property of metal ion catalyzed Luc/GO-H_2O_2 CL reaction

The catalytic effect of various metal ions such as Co^{2+}, Ni^{2+}, Mn^{2+}, Pb^{2+} and Cu^{2+} on the CL reaction of Luc/GO with H_2O_2 in alkaline solution was investigated by simply mixing different metal ions with Luc/GO. 10 μL of 0.5 mM metal ions was mixed into 1 mL as-prepared Luc/GO. Then 200 μL 10 mM H_2O_2 in 0.1 M NaOH was injected into above solution. CL signal was measured with a BPLC luminometer and PMT voltage was set at -600 V.

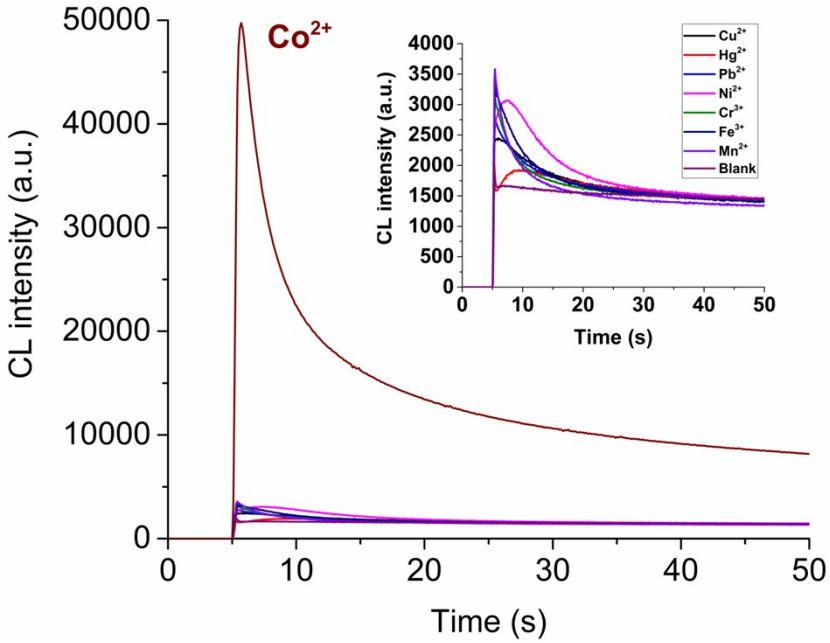

Fig. S1. CL kinetic curves for reaction between Luc/GO and different metal ions (Co^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Cr^{3+}, Fe^{3+}, and Mn^{2+}). The inset is the magnification.

S2. Optimization of experimental conditions

The experimental conditions for the synthesis of $Co(Trp)_2$/Luc/GO from Luc/GO were optimized. The CL intensity of $Co(Trp)_2$/Luc/GO increased with the increase of the temperature when assembled $Co(Trp)_2$ onto Luc/GO. It was due to that more $Co(Trp)_2$ complexes could be adsorbed onto the surface of Luc/GO result from the thermodynamic equilibrium result. However, when the temperature was higher than 40 ºC, the stability of $Co(Trp)_2$/Luc/GO decreased. Meanwhile, the best interaction reaction time for the assembly of $Co(Trp)_2$ onto Luc/GO was about 6 hours. In addition, the integral value of the CL intensity over 10 seconds increased with the increase of the concentration of $Co(Trp)_2$ from 50 μM to 100 μM. However, the CL signal decreased when the concentration of $Co(Trp)_2$ was above 50 μM. The concentration of $Co(Trp)_2$ was optimized around 50 μM.

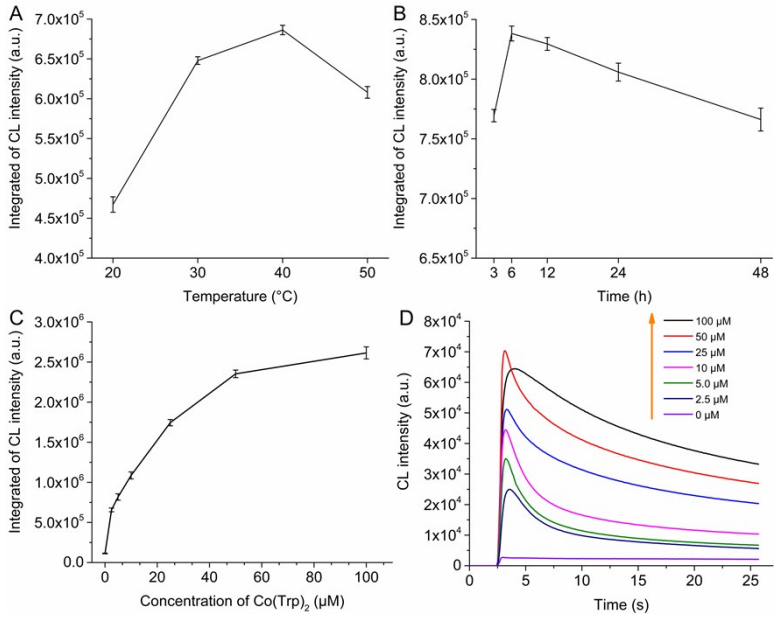

Fig. S2. Optimization of the conditions of synthetic $Co(Trp)_2$/Luc/GO from Luc/GO, (A) temperature, (B) time, (C) concentration of $Co(Trp)_2$ and (D) CL behavior of $Co(Trp)_2$/Luc/GO prepared with different concentration of $Co(Trp)_2$. 200 μL 10 mM H_2O_2 in 0.1 M NaOH was injected into $Co(Trp)_2$/Luc/GO. CL signal was measured with a BPLC luminometer and PMT voltage was set at -600 V.

S3. Characterization of $Co(Trp)_2$/Luc/GO hybrids

HRTEM Characterization of $Co(Trp)_2$/Luc/GO hybrids

The specimen of HRTEM was prepared by dropping the sample on to a copper net covered by a carbon film.

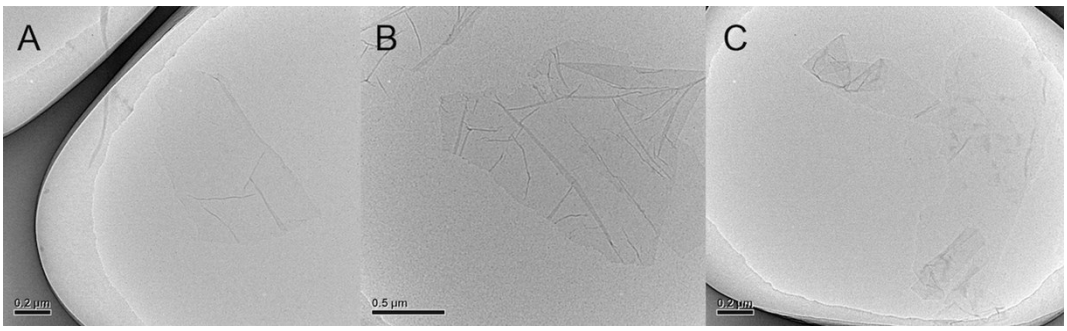

Fig. S3. TEM images of (A) GO, (B) Luc/GO and (C) $Co(Trp)_2$/Luc/GO.

Determination of lucigenin concentration in Luc/GO hybrids

The concentration of lucigenin in Luc/GO hybrids was determined by FL analysis. 100 μL different concentrations of lucigenin (1-50 μM) was added into 900 μL supernatant of GO centrifuged at a speed of 15,000 rpm for 10 min. The FL intensity of above solutions was recorded at 490 nm (ex: 262 nm). The results indicated that the FL intensity increased linearly with the increase of lucigenin concentration as shown in Fig. S4. The regression equation is $I = 10.488 + 45.431 \times C$ with a regression coefficient of 0.9978. 100 μL ultrapure water was added into 900 μL supernatant of Luc/GO centrifuged at a speed of 15,000 rpm for 10 min, and recorded the FL intensity at the same condition. The amount of lucigenin absorbed on the GO surface approximately equals to that the synthetic lucigenin concentration subtracts the concentration of free lucigenin in the supernatant, which was calculated as about 4 μM.

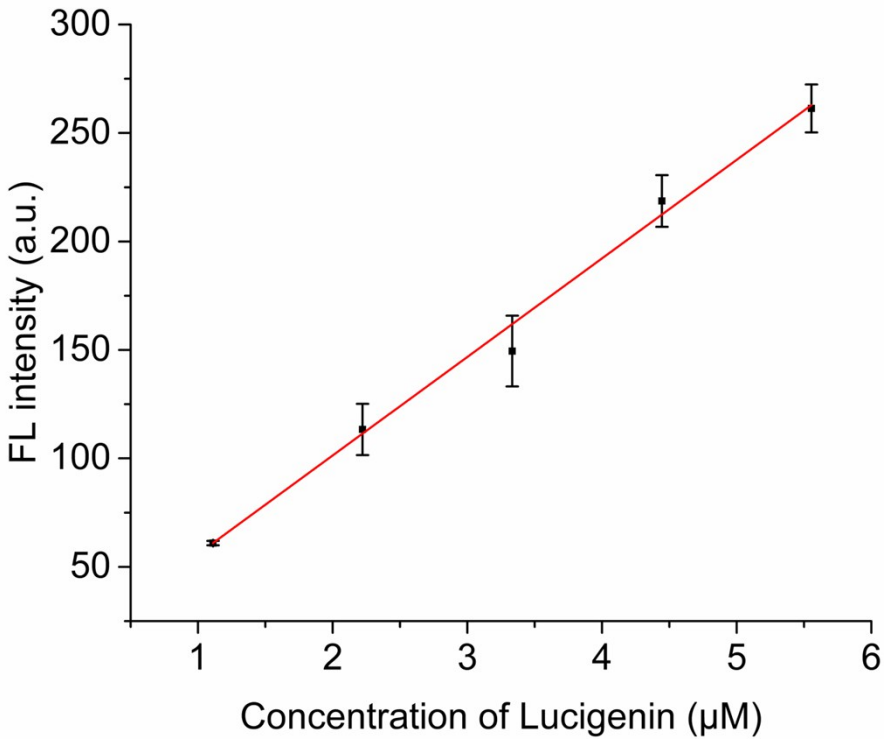

Fig. S4. Calibration curve for lucigenin concentration.

XPS characterization of $Co(Trp)_2$/Luc/GO

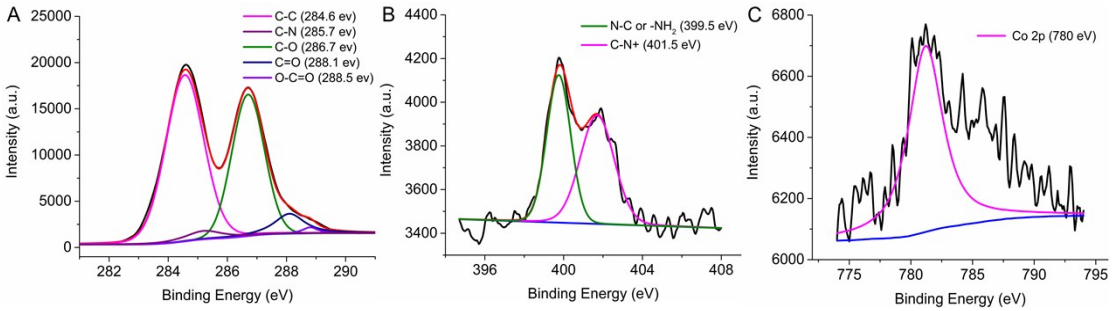

Fig. S5. XPS spectrum of (A) C 1s, (B) N 1s, (C) Co 2p from $Co(Trp)_2$/Luc/GO.

S4. CL mechanism of $Co(Trp)_2$/Luc/GO-H_2O_2 in alkaline solution

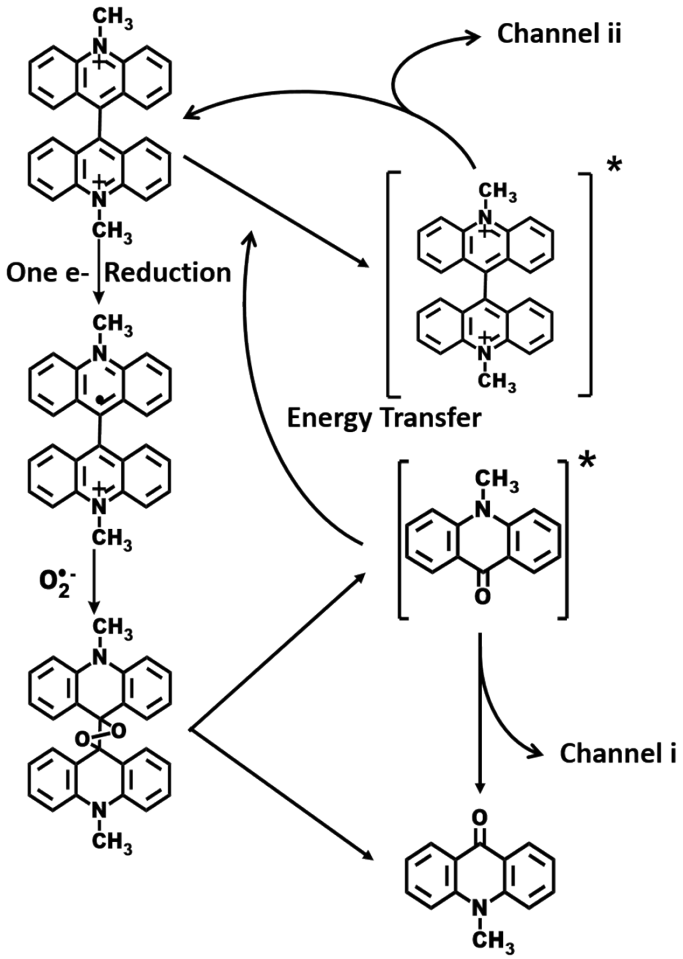

Fig.. S6. CL reaction pathways of lucigenin-H_2O_2 in alkaline solution.

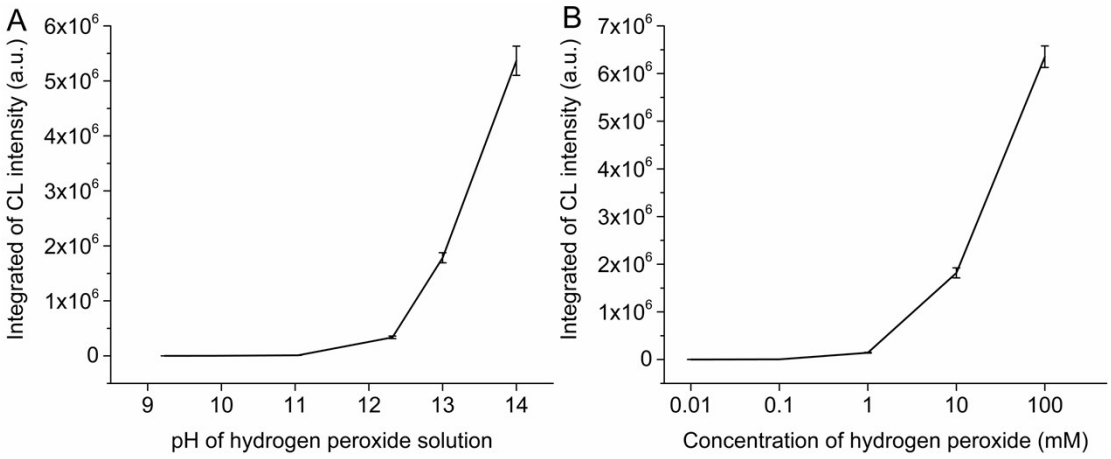

Fig. S7. Effect of pH (A) and (B) concentration of H_2O_2 on CL intensities of $Co(Trp)_2$/Luc/GO. CL measurement: a BPLC luminometer at -600 V PMT.