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$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$ 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.

![CL kinetic curves for reaction between Luc/GO and different metal ions](image)

**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 °C, 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$_2$O$_2$ 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.

![Figure S3](image)

**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$_2$O$_2$ in alkaline solution

Fig. S6. CL reaction pathways of lucigenin-H$_2$O$_2$ in alkaline solution.

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