Electronic Supplementary Information

Hydroxylamine-*O*-sulfonic acid as an efficient coreactant of luminol chemiluminescence for selective and sensitive detection

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EXPERIMENTAL SECTION

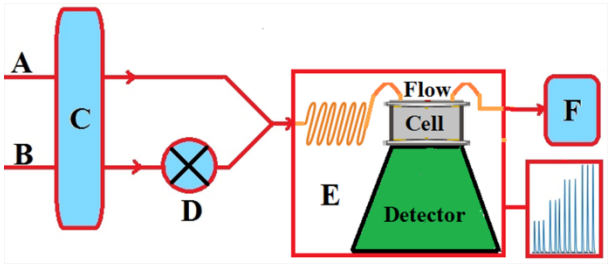
Chemicals and materials. Luminol and hydrogen peroxide were obtained from Beijing Chemical Reagent Company. HOSA was purchased from Ourchem Chemical Reagent Co., Ltd. (China). $CoCl_2 \cdot 6H_2O$ was obtained from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). Luminol stock solution (10 mM) was prepared by dissolving 0.1772 g luminol in 0.10 M NaOH and then dilute with water to 100 mL. Luminol working solutions with different pH values were prepared by diluting the luminol stock solution with carbonate buffer or sodium hydroxide. HOSA solution was prepared by directly dissolving HOSA in water. Other chemicals were analytical reagent grade and used as received. Doubly distilled water was used throughout all experiments.

Apparatus. The CL intensities were measured by a flow injection CL system consisting of a IFIS-C mode intelligent flow injection sampler (ReMax Inc., Xi'an, China), a BPCL ultra-weak luminescence analyzer (Institute of Biophysics, Chinese Academic of Sciences), and a home-made flow cell. The flow cell was put in a light-tight box of the luminescent analyzer. The loop injector was equipped with an injection loop of 50 μL.

Procedure of HOSA detection. Scheme 1 shows the schematic diagram of the flow system for HOSA detection. 10 μM luminol in 0.10 M carbonate buffer solution (pH 11.45) and water were respectively pumped into the flow cell through channels A and B at a flow rate of 1.25 mL/min. Different concentrations of HOSA in water were injected through the loop injector.

Procedure of luminol detection. 2 mM HOSA in water and 0.10 M carbonate buffer solution (pH 11.45) were respectively pumped into the flow cell through channels A and B at a flow rate of 1.25 mL/min. Different concentrations of luminol were injected through the loop injector.

Procedure of Co^{2+} detection. 2 mM HOSA in water and carbonate buffer solution (pH 11.45) were respectively pumped into the flow cell through channels A and B at a flow rate of 1.25 mL/min. Different concentrations of Co^{2+} were mixed with 10 μM luminol first, and then the mixture were injected through the loop injector.



Scheme S1 A schematic diagram of the flow system for this new luminol CL system. A and B: flow channels; C: IFIS-C mode intelligent flow injection sampler; D: loop injector; E: CL detector; F: waste cup.

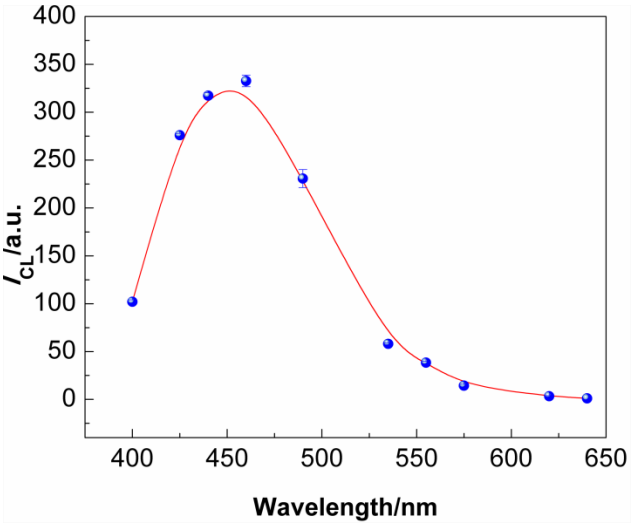


Fig. S1 CL spectrum of luminol/HOSA system. *c*(luminol): 10 μM; *c*(HOSA): 2 mM; Photomultiplier tube voltage: 800 V.

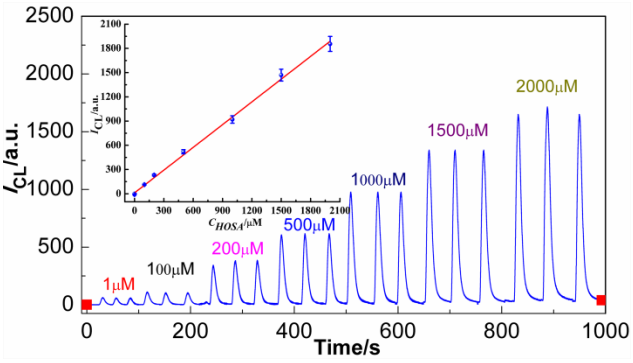
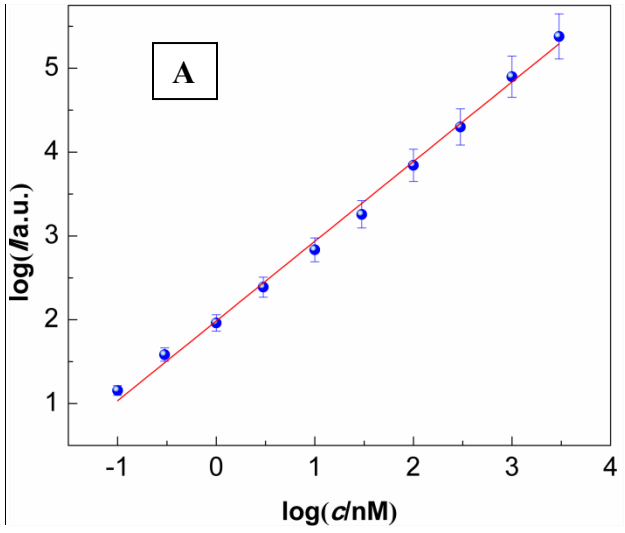


Fig. S2 CL profiles of luminol-HOSA system in the presence of different concentrations of HOSA. Inset: linear relationship between CL intensity and the concentration of HOSA from 1 to 2000 μM. c(luminol):10 μM; photomultiplier tube voltage: 800 V.



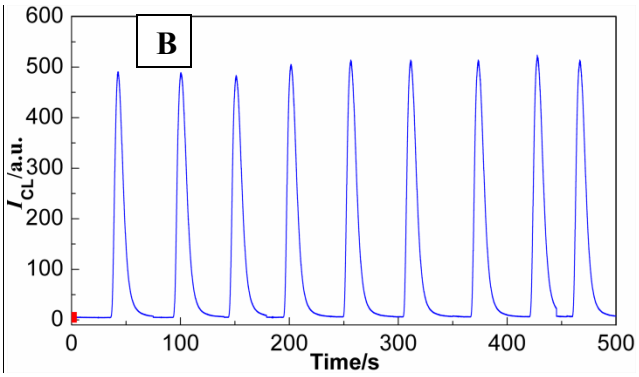


Fig. S3 (A) Linear relationship between CL intensity (log *I*) and the concentration of luminol (log *c*) from 0.1 to 3000 nM. **(B)** The CL intensity-time curves at the luminol concentration of 500 nM. *c*(HOSA):2 mM; photomultiplier tube voltage: 1000 V.

Table S1. Comparison of Different Methods for the Detection of Cobalt ions

Analytical Method	Probe	Detection Limit
Luminescence	Ag NCs	100nM[7]
Absorbance	*P*-Au NPs[a]	2000nM[5]
Absorbance	CF-CdS QDs[b]	390nM[4]
SERS	DTC -Ag NPs[c]	1.0nM[6]
Chemiluminescence	CTAB@C-dots	0.67nM[8]
Photoluminescence	C-dots	5.0nM[3]
Photoluminescence	Mn-d ZnS QDs	60nM[2]
Photoluminescence	TGA-CdTe QDs[d]	7.3nM[1]
CL (Present Work)	Probe-free	0.13nM

[a]Peptide modified Au NPs. [b]Carboxyl-functionalized CdS quantum dots (QDs). [c]Dithiocarbamate anchored terpyridine (TPY-DTC) functionalized Ag NPs. [d]Thioglycolic acid (TGA)-capped CdTe QDs.

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