

Supplementary Information

Engineered Co_3O_4 Nanoboxes Boost Luminol Chemiluminescence for Selective Mn^{2+} Sensing

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Chemicals

Co(NO₃)₂•6H₂O, 3,3,5,5'-tetramethyl-benzidine (TMB) and 2-methylimidazole (2-MIm) were purchased from Aladdin (Shanghai, China). Tannic acid, luminol, superoxide dismutase (SOD) and NaN₃ were purchased from Sinopharm Chemical Reagent Co., Ltd, Ark Pharm (Illinois, USA), and Beijing HWRK Chem. Co., Ltd (Beijing, China) and Tianjin Fuchen Chemical Reagent Factory (Tianjin, China), respectively. MnSO₄•H₂O, KCl, CaCl₂, MgSO₄, CuSO₄•5H₂O, and H₂O₂ were supplied by Beijing Chemical Works (Beijing, China). NaCO₃ anhydrous and NaHCO₃ were purchased from Beijing Beihua Fine Chemicals Co., Ltd (Beijing, China). Thiourea and Cr(NO₃)₃•9H₂O were supplied from Xilong Chemical Co., Ltd. (Guang dong, China). Luminol (10 mM) was prepared using a 0.10 M NaOH aqueous solution and kept at 4 °C in a dark-coloured bottle for two weeks prior to use. Carbonate buffer solutions (CBS, 0.10 M) in different pH levels were prepared with NaCO₃ and NaHCO₃ and adjusted using 1.0 M NaOH. All chemicals employed were of analytical grade, and the experimental solutions were prepared with ultrapure water from the Millipore system (18.2 MΩ•cm⁻¹). All analytical grade chemicals received were from standard suppliers and were not further purified.

Instruments

The CL emissions were recorded using a BPCL ultraweak chemiluminescence analyzer (Institute of Biophysics, Chinese Academy of Sciences) equipped with a high-precision peristaltic sampler BT100M (Baoding Chuang Rui Precision Pump Co., Ltd.) operated within a flow injection analysis-CL system (FIA-CL). A home-made three-channel CL flow cell was placed in a dark box of the luminescent analyzer. The CL emission signals were detected by a photomultiplier tube (PMT, Hamamatsu CR-131), set at -500 V working voltage and then recorded to a computer equipped with a data acquisition interface.

Ultraviolet-visible (UV-Vis) absorption spectra were collected using a UV1800 UV-Vis spectrometer (Shimadzu, Japan). The CL emission spectrum was measured with an RF-5301PC spectrofluorometer (SHIMADZU, Japan) operated at a 1.5 nm slit-width in high-speed scanning mode after switching into CL mode, and the excitation wavelength was set to 350 nm to record the CL intensities. The morphology of the sample crystals was examined using scanning electron microscopy (SEM, JEOL JSM-6700F) and a Field emission transmission electron microscope (FETEM, Hitachi H-600, Japan) operated at 5.0 kV and 100 kV, respectively. X-ray photoemission spectroscopy (XPS) spectra were measured using a ThermoFisher ESCALAB Xi+ spectrometer equipped with an Al Kα X-ray source. The X-ray diffraction patterns of powder samples were measured using a Bruker D8 ADVANCE diffractometer equipped with Cu Kα (λ = 0.154 nm) radiation filter.



Scheme S1. Digitally captured images showing the chemical etching procedure for ZIF-67 MOF modification.

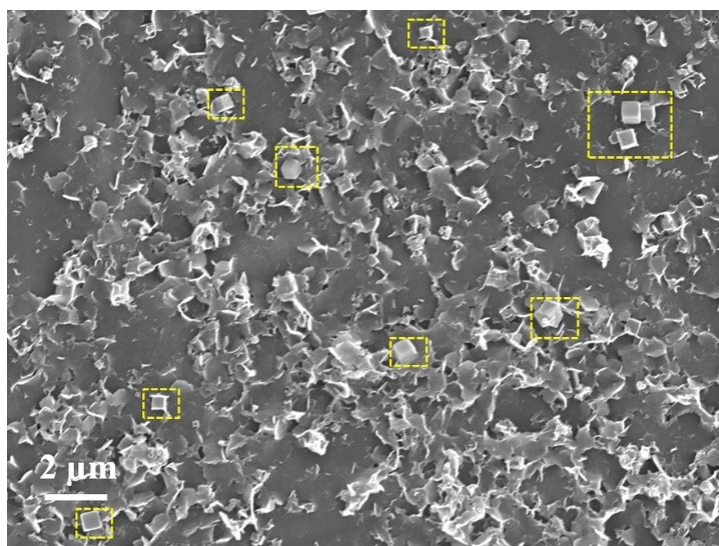


Fig. S1 SEM images of TA-Co complex NBs.

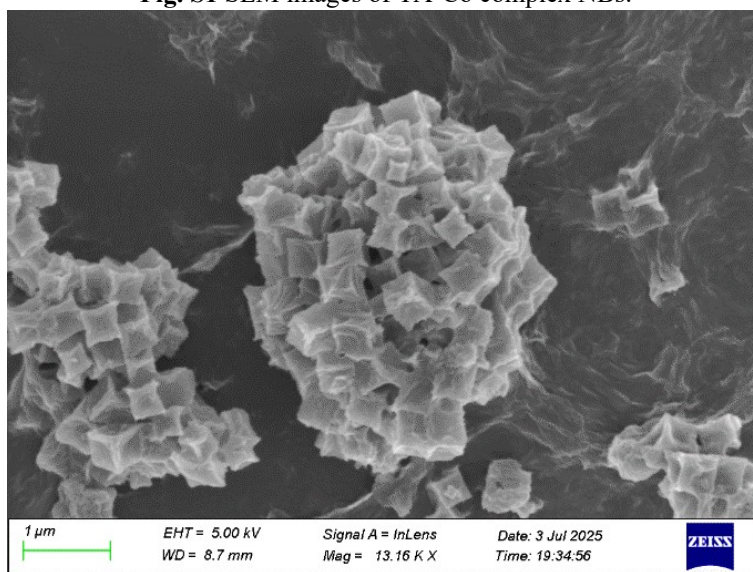


Fig. S2 SEM images for TA-unmodified Co_3O_4 .

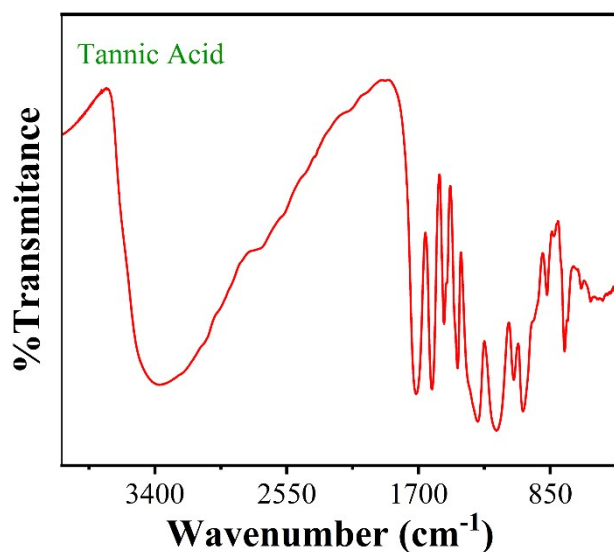


Fig. S3 FT-IR spectrum of TA.

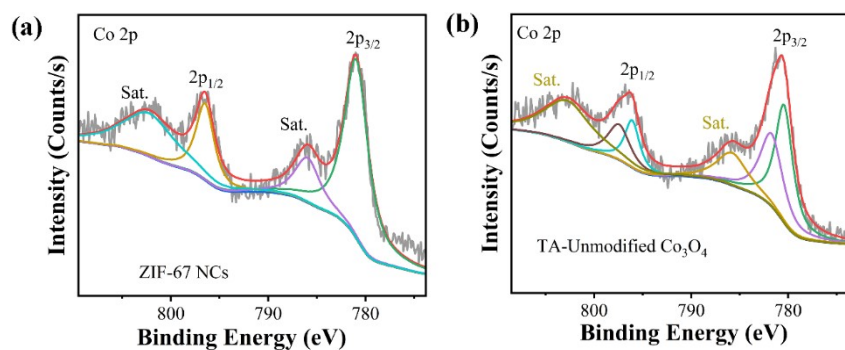


Fig. S4 Co 2p high-resolution XPS deconvoluted spectra of (a) ZIF-67 NCs and (b) TA-unmodified Co_3O_4 .

Optimisation of Chemiluminescence Conditions

The CL signal intensity was examined across variable pH levels ranging from 9.2 to 11.5 (Fig. S4a). The CL signal increased with rising pH and slowly declined after pH 10.5. This increase in signal results from luminol deprotonation at higher pH and may generate side reaction products at extreme pH levels, potentially quenching the CL intensity. The effect of H_2O_2 concentrations on the CL signal was also analyzed (Fig. S4b). The CL signal increased from 10 to 50 μM H_2O_2 but appeared to change slope after 50 μM . Meanwhile, the background signal was higher, making it difficult to produce reproducible CL signals. Therefore, 50 μM H_2O_2 was chosen as the optimal test condition for subsequent analysis. Additionally, luminol is the rate-determining reagent in the CL reaction. The signal strength increased with a similar slope up to 5 μM luminol and showed minimal change after 10 μM , indicating that 5 μM is the optimal luminol concentration for the test condition (Fig. S4c). Finally, we examined the effect of Co_3O_4 NBs nanozyme concentration on the luminol/ H_2O_2 CL system (Fig. S4d). The signal intensity increased as the material concentration increased. However, the signal gradually levelled after 15 $\mu\text{g/mL}$, as the optimal diffusion of reagents into the exposed surface active sites is reached. Therefore, the optimized test conditions are pH 10.5, 50 μM H_2O_2 , 5 μM luminol, and 15 $\mu\text{g/mL}$ Co_3O_4 NBs.

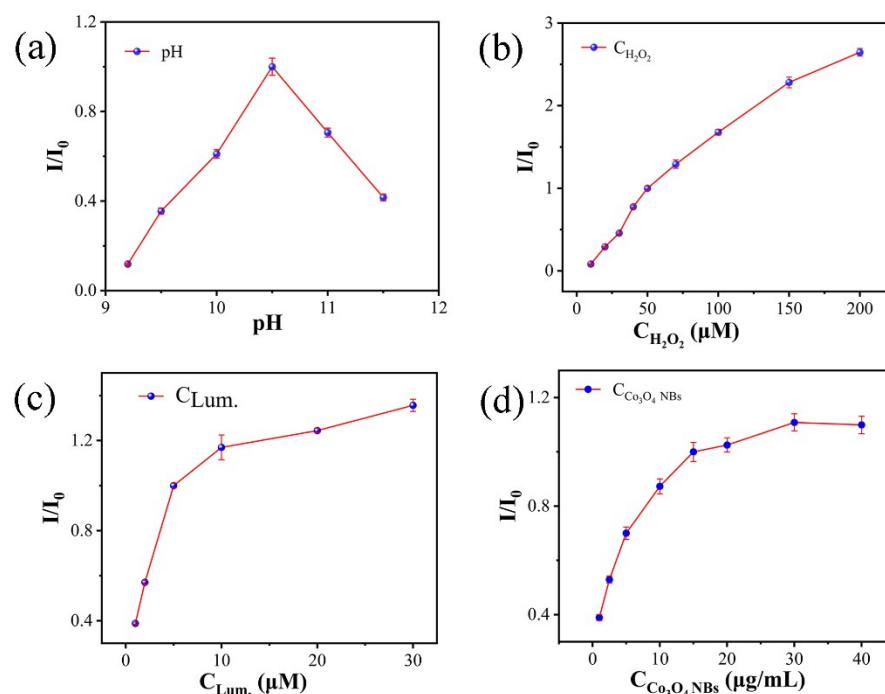


Fig. S5 Optimization of experimental conditions. (a) optimisation of pH (the concentration of H_2O_2 , luminol and Co_3O_4 NBs were 50 μM , 10 μM and 15 $\mu g/mL$ respectively, $n=3$), (b) optimisation of H_2O_2 concentrations (pH, the concentration of H_2O_2 and Co_3O_4 NBs were 10.5, 10 μM and 15 $\mu g/mL$ respectively, $n=3$), (c) optimisation of luminol concentrations (pH and the concentration of H_2O_2 and Co_3O_4 NBs were 10.5, 50 μM and 15 $\mu g/mL$ respectively, $n=3$), (d) optimisation of Co_3O_4 NBs dosage (pH, the concentration of H_2O_2 , and luminol were 10.5, 50 μM and 5 μM respectively, $n=3$).

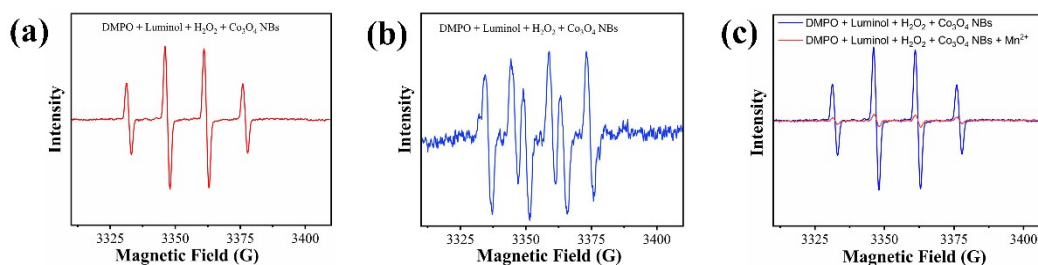


Fig. S6 Electron spin resonance (ESR) spectra of (a) $DMPO \cdot OH$ for luminol/ H_2O_2 / Co_3O_4 NBs, (b) $DMPO-O_2^{\cdot-}$ for luminol/ H_2O_2 / Co_3O_4 NBs, and (c) $DMPO \cdot OH$ for luminol/ H_2O_2 / Co_3O_4 NBs in the absence of Mn^{2+} (blue line) and in the presence of Mn^{2+} (red line). Conditions: DMPO (20 mM), luminol (5 μM), H_2O_2 (50 μM), Co_3O_4 NBs (15 $\mu g/mL$) and Mn^{2+} (20 μM).

Table S1. Detection of Mn²⁺ ion in real drinking water samples.

Sample	Concentration (μM)		Recovery (%)	RSD (%), n=3
Drinking water	Spiked	Detected		
	0	ND	-	-
	0.5	0.487	97.40	0.71
	0.8	0.869	108.6	4.7
	1.5	1.34	89.5	1.8