Electronic Supplementary Information

Mesoporous materials-based manipulation of the enzyme-like activity of $CoFe_2O_4$ nanoparticles

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Experimental Section

Materials: All chemicals used in this work were of analytical grade and used as received without further purification. Luminol was from Merck (Germany), a 0.01 mol L^{-1} luminol solution was prepared by dissolving 1.772 g luminol in 1000 mL of 0.01 mol L^{-1} NaOH solutions. γ-Al_2O_3 and SiO_2 were from Sigma-Aldrich. The SBA-15 was prepared according to the method reported by Zhao et al.[2] 3,3,5,5-tetramethylbenzidine (TMB) was purchased from Sigma-Aldrich (St. Louis, MO) and stored in a refrigerator at 4 °C. H_2O_2, sodium carbonate, sodium hydrogen carbonate, sulfuric acid, hydrochloric acid, sodium hydroxide, acetic acid, sodium acetate, citrate acid and sodium citrate were obtained from Chongqing Chemical Reagents Company (Chongqing, China). All glassware was soaked in 10% nitric acid and thoroughly cleaned before use. Ultra pure water prepared in the lab was used throughout. The $CoFe_2O_4$ MNPs were prepared according to the method of Massart et al.[1] The size of the as-synthesized $CoFe_2O_4$ NPs was characterized by a model Philips Tecnai 10 transmission electron microscope (TEM, Philips) and the average diameter of the prepared $CoFe_2O_4$ NPs was 14 ± 2 nm.

Preparation of SBA-15, SiO_2 and Al_2O_3 supported $CoFe_2O_4$ MNPs: The coated $CoFe_2O_4$ MNPs was prepared by adding 0.02 g SBA-15 (or 0.05 g SiO_2 and Al_2O_3) and 5 mL of 1.07 mg mL^{-1} $CoFe_2O_4$ MNPs into a 50 mL beaker, then 5 mL of 0.1 mol L^{-1} sulfuric acid was added slowly to the beaker, the mixture was stirred for 5 h at room temperature. The obtained solution was diluted to 50 mL and stored at room temperature for further use.

Instrumentation: CL measurements were performed on a MCFL-A Multifunction Chemiluminescence/Bioluminescence Analyzer (Ruike Electronic Equipment Company Ltd., Xi'an, China). The pH of the solutions was detected by a PHS-3D pH meter (Shanghai Precision Scientific Instruments Co., Ltd., China); The CL spectra were recorded on an F-4500 spectrofluorimeter (Kyoto, Japan) under the model of fluorescence scan by turning off the excitation light. UV−visible measurements were performed on a UV−2450 Shimazhu spectrophotometer (Shuzhou, China). The zeta potential was measured by Zetasizer Nano ZS90 apparatus (Malvern, UK). The scanning transmission electron microscopy (SEM) images were taken on Hitachi model S-4800 field emission scanning electron microscope (Hitachi, Japan), with an accelerating voltage of 5 to 20 kV. The N_2 adsorption–desorption isotherms were performed on a Quantachrome Autosorb Automated Gas Sorption System (Quantachrome Instruments, America). The microscope images were obtained on an Olympus IX70 Inverted Fluorescence Microscope (Olympus America Inc.). The size distribution was performed by counting 100 particles.

CL analysis: The CL intensity was measured by a flow injection CL system. Two peristaltic pumps (30 r min^{-1}, Longfang Instrument Factory, Wenzhou, China) were used to deliver all solutions; one for delivering catalyst solution and water carrier stream; the other for delivering CL reaction reagents. PTFE tubing (0.8 mm i.d.) was used to connect all components in the flow system. For CL measurement, flow lines were inserted into the luminol solution, water, and $CoFe_2O_4$ MNPs or supported $CoFe_2O_4$ MNPs solution, respectively. Then the pumps were started at flow rate of 3 mL min^{-1} (per tube) until a stable baseline was recorded. Injection was made by using an eight-way injection valve equipped with a 200 μL sample loop. The CL signal produced was detected by a photomultiplier tube (operated at −500 V), then recorded by a computer, equipped with a data acquisition interface. Data acquisition and treatment were performed with REMAX software running under Windows XP. All results were performed in triplicate, and the data were recorded as a mean.

References

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Table S1 Surface features of the supports

Support	Surface area ($m^2\ g^{-1}$)	Pore diameter (nm)	Pore volume ($cm^3\ g^{-1}$)
Al_2O_3	183.8	4.47	0.24
SBA-15	320.2	5.85	0.43
SiO_2	354.5	13.40	1.04

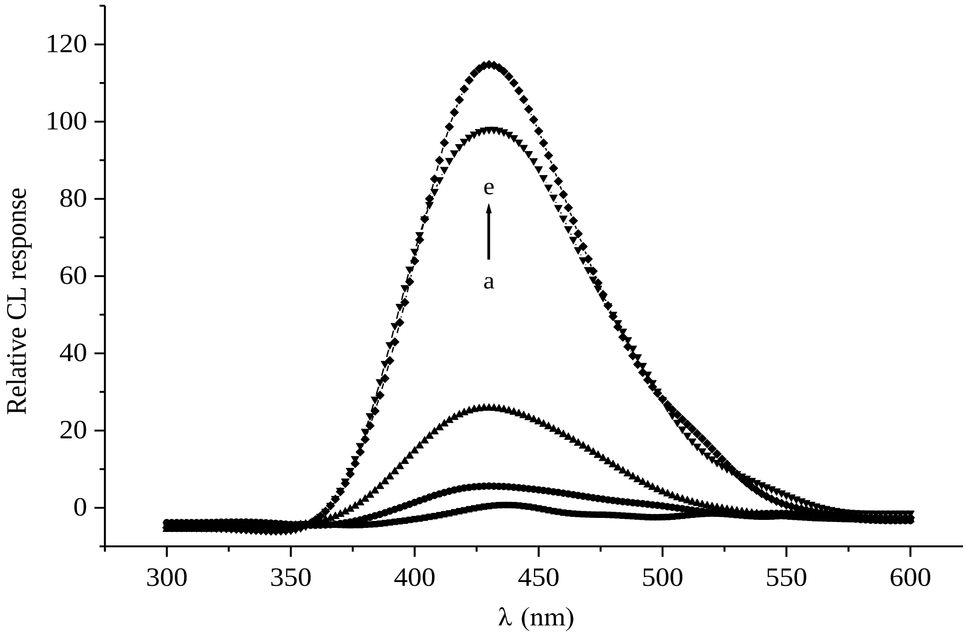

Fig. S1. CL spectra for the luminol−$CoFe_2O_4$ system. (a): luminol solution; (b): $CoFe_2O_4$+luminol; (c): SBA-15 supported $CoFe_2O_4$+luminol; (d): SiO_2 supported $CoFe_2O_4$+luminol; (e): Al_2O_3 supported $CoFe_2O_4$+luminol. Conditions: luminol concentration: 1.0×10^{-5} mol L^{-1} in 0.1 mol L^{-1} Na_2CO_3−$NaHCO_3$ buffer (pH 11.7); $CoFe_2O_4$ concentration: 2.14 mg L^{-1}; SBA-15, SiO_2, Al_2O_3 supported $CoFe_2O_4$ were made by 2.14 mg L^{-1} $CoFe_2O_4$ and 8 mg L^{-1} SBA-15, 20 mg L^{-1} SiO_2, and 20 mg L^{-1} Al_2O_3, respectively.

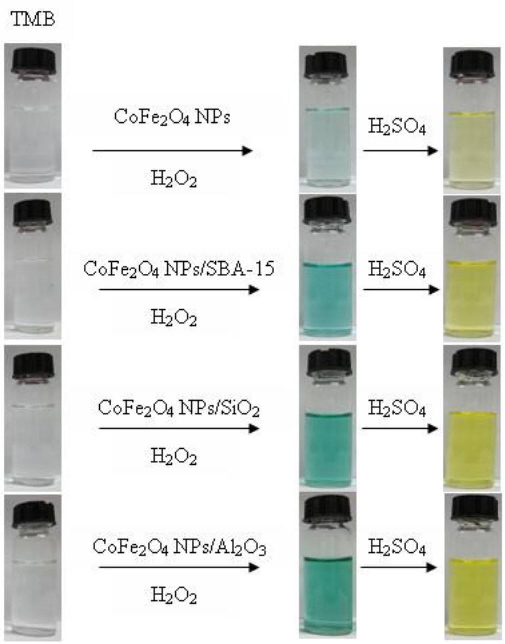

Fig. S2. Images of oxidation color reaction of TMB by H_2O_2 after catalyzing by $CoFe_2O_4$ or supported $CoFe_2O_4$ at pH 3.5 (0.2 mol L^{-1} acetate buffer) and subsequently being quenched by H_2SO_4. Conditions: TMB concentration : 5.0×10^{-5} mol L^{-1}; H_2O_2 concentration: 5.0×10^{-3} mol L^{-1}; H_2SO_4 concentration: 2.0 mol L^{-1}; $CoFe_2O_4$ concentration: 6.42 mg L^{-1}; SBA-15, SiO_2, Al_2O_3 supported $CoFe_2O_4$ were made by 2.14 mg L^{-1} $CoFe_2O_4$ and 8 mg L^{-1} SBA-15, 20 mg L^{-1} SiO_2, and 20 mg L^{-1} Al_2O_3, respectively.

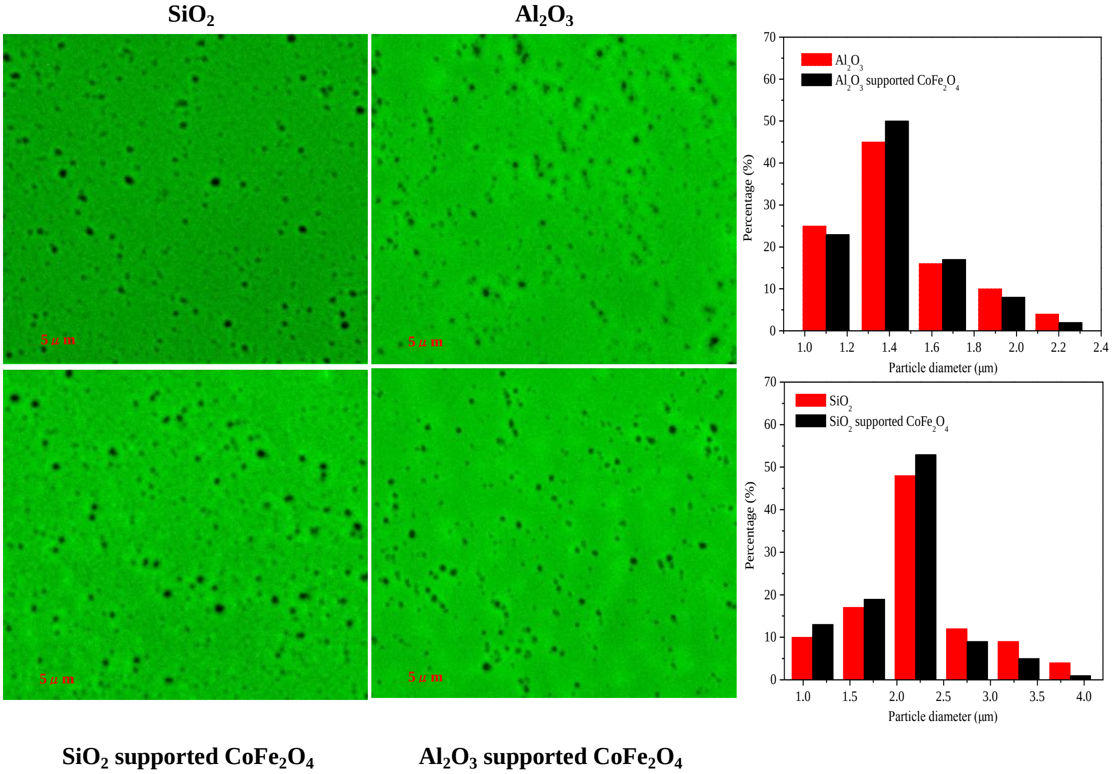

Fig. S3A. Microscope images and particle size distribution (right) of uncoated and coated SiO_2 and Al_2O_3 supported $CoFe_2O_4$.

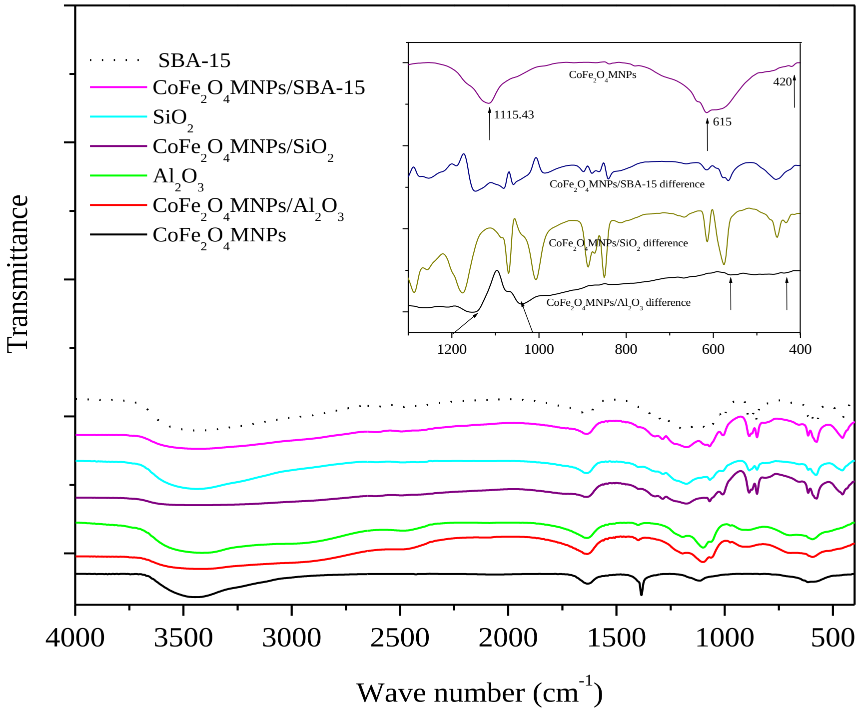

Fig. S3B. The FT-IR spectra of support, $CoFe_2O_4$, and $CoFe_2O_4$-coated support. Inset: The difference spectrum between $CoFe_2O_4$-coated support and uncoated support.

The FT-IR spectra in Fig. S3B suggest that the positions and the relative intensities of the bands for the supported complexes are very similar to that of support. For example, for SBA-15 supported $CoFe_2O_4$, the absorption band at 1176 cm^{-1} is assigned for asymmetric Si–O–Si stretching mode. The band at 1069 cm^{-1} corresponds to Si–O–H stretching mode. The bands at 887 and 850 cm^{-1} correspond to Si–O–Si symmetric stretching vibration mode. The absorption band at 577 corresponds to Si–O–Si and O–Si–O bending mode.[1] For $CoFe_2O_4$ MNPs, the band at 1115 cm^{-1} is corresponds to the Fe-Co alloys system. The bands at 570 ~ 615 and 420 cm^{-1} are respectively attributed to the Fe–O and Co–O vibrational modes (The 1384 cm^{-1} peak reveals existence of the NO_3^- impurity in the $CoFe_2O_4$ sample).[2,3] The difference spectra between $CoFe_2O_4$-coated support and uncoated support showed characteristic $CoFe_2O_4$ absorption bands despite the weak signal as a result of the low $CoFe_2O_4$ concentration, suggesting unambiguously that $CoFe_2O_4$ was coated on the supports surface. It is noted that the Fe–O stretching band was found to shift from 615 to 566, 567 and 560 cm^{-1}, the Co–O stretching band was found to shift from 420 to 456, 454 and 450 cm^{-1}, respectively.

References

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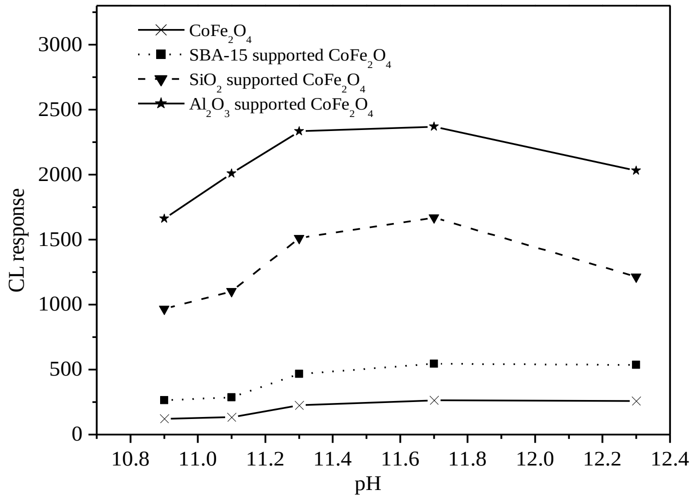


Fig. S4. pH optimization of the luminol solution on the CL response. Conditions: luminol: 2.0×10^{-6} mol L^{-1}; 0.1 mol L^{-1} Na_2CO_3–$NaHCO_3$ buffer; $CoFe_2O_4$: 2.14 mg L^{-1}; SBA-15, SiO_2, Al_2O_3 supported $CoFe_2O_4$ were made by 2.14 mg L^{-1} $CoFe_2O_4$ and 8 mg L^{-1} SBA-15, 20 mg L^{-1} SiO_2, and 20 mg L^{-1} Al_2O_3, respectively.

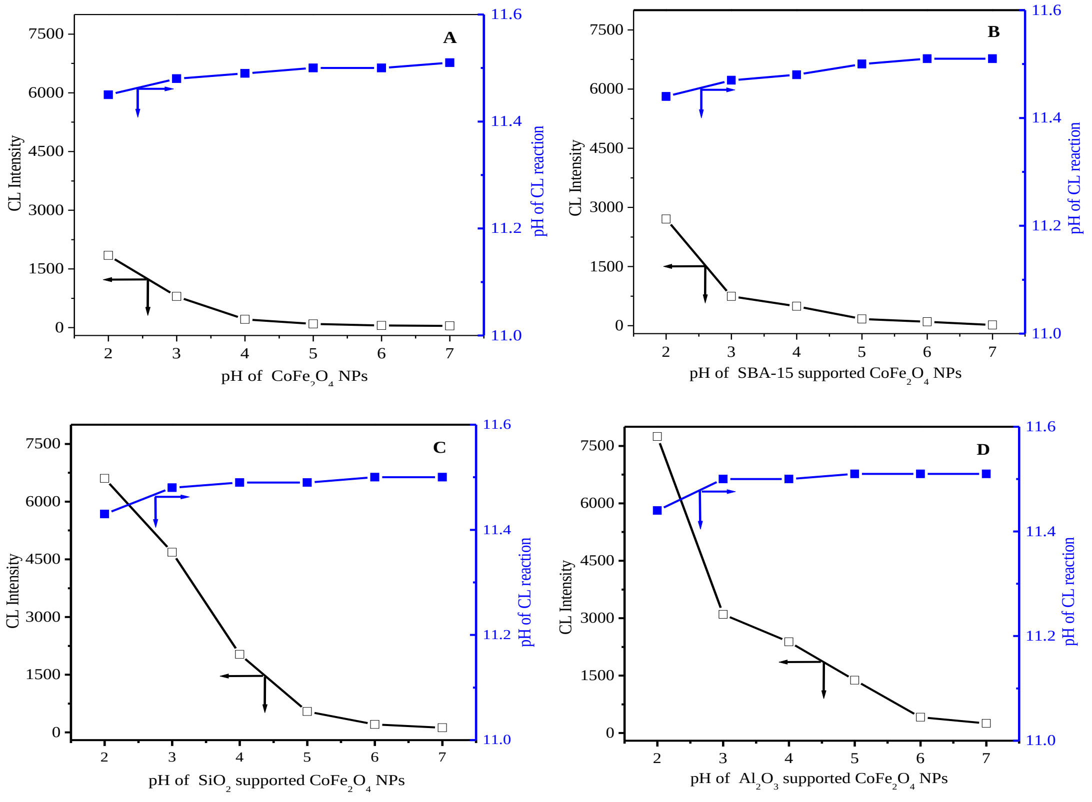


Fig. S5. The variations of the CL response and the pH of the CL reaction with pH of $CoFe_2O_4$ NPs (A), SBA-15 supported $CoFe_2O_4$ NPs (B), SiO_2 supported $CoFe_2O_4$ NPs (C) and Al_2O_3 supported $CoFe_2O_4$ NPs (D). Conditions: 2.0×10^{-6} mol L^{-1} luminol in 0.1 mol L^{-1} Na_2CO_3–$NaHCO_3$ buffer (pH 11.7); $CoFe_2O_4$ concentration: 2.14 mg L^{-1}; SBA-15, SiO_2, Al_2O_3 supported $CoFe_2O_4$ were made by 2.14 mg L^{-1} $CoFe_2O_4$ and 20 mg L^{-1} SiO_2, 20 mg L^{-1} Al_2O_3, and 8 mg L^{-1} SBA-15, respectively.

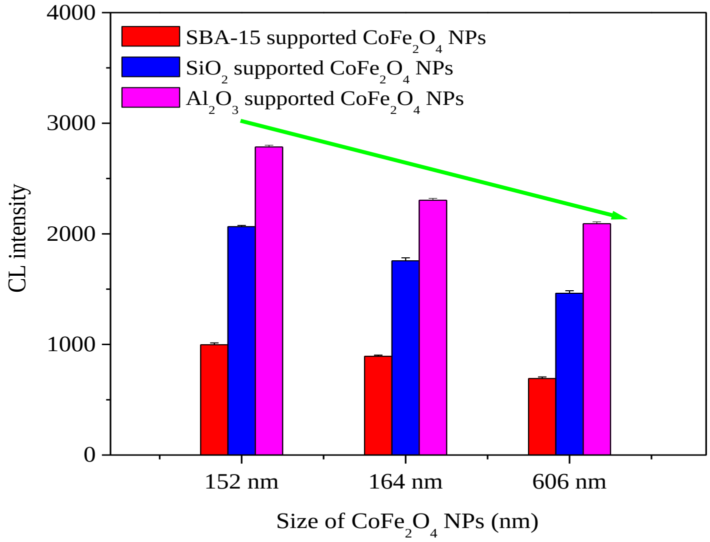
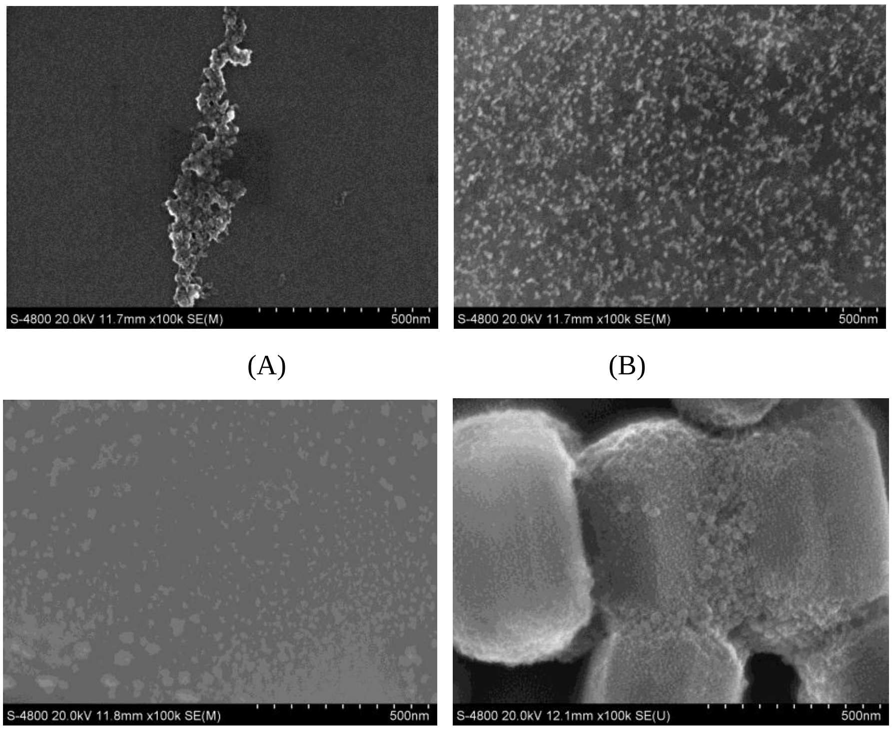


Fig. S6. Effects of CoFe$_2$O$_4$ NPs size on the CL intensity. Conditions: 2.0×10^{-6} mol L^{-1} luminol in 0.1 mol L^{-1} Na$_2$CO$_3$–NaHCO$_3$ buffer (pH 11.7); CoFe$_2$O$_4$ concentration: 2.14 mg L^{-1}; SBA-15, SiO$_2$, Al$_2$O$_3$ supported CoFe$_2$O$_4$ were made by 2.14 mg L^{-1} CoFe$_2$O$_4$ and 8 mg L^{-1} SBA-15, 20 mg L^{-1} SiO$_2$, and 20 mg L^{-1} Al$_2$O$_3$, respectively.



(A) (B)

(C) (D)

Fig. S7. SEM images of the CoFe$_2$O$_4$ NPs (A), SiO$_2$ supported CoFe$_2$O$_4$ NPs (B), Al$_2$O$_3$ supported CoFe$_2$O$_4$ NPs (C), and SBA-15 supported CoFe$_2$O$_4$ NPs (D).

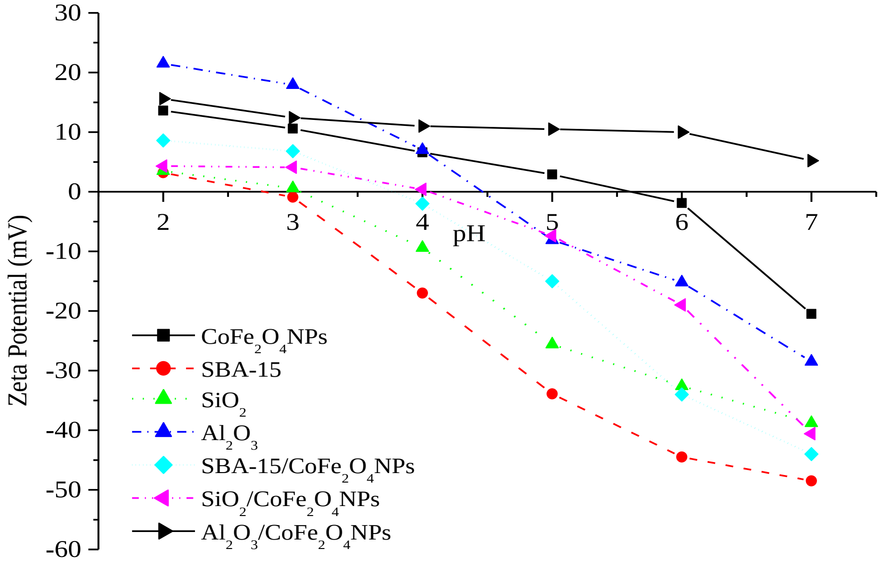


Fig. S8. Variation of the zeta-potential under different pH value. Conditions: $CoFe_2O_4$ concentration: 2.14 mg L^{-1}; SBA-15, SiO_2, Al_2O_3 concentration: 8 mg L^{-1}, 20 mg L^{-1}, and 20 mg L^{-1}, respectively. SBA-15, SiO_2, Al_2O_3 supported $CoFe_2O_4$ were made by 2.14 mg L^{-1} $CoFe_2O_4$ and 20 mg L^{-1} SiO_2, 20 mg L^{-1} Al_2O_3, and 8 mg L^{-1} SBA-15, respectively.

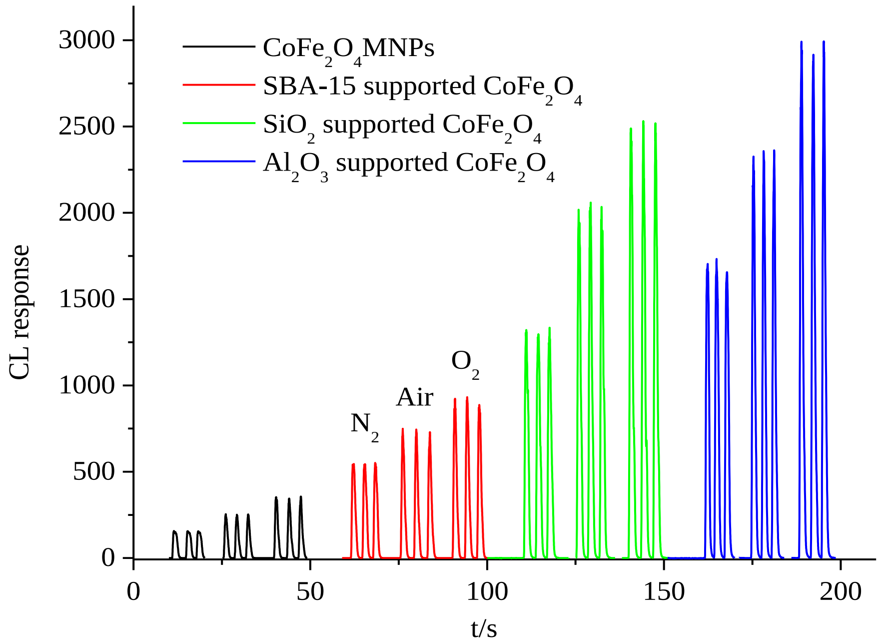


Fig. S9. Effects of nitrogen and oxygen on the CL intensity. Conditions: luminol concentration: 2.0×10^{-6} mol L^{-1} in 0.1 mol L^{-1} Na_2CO_3–$NaHCO_3$ buffer (pH 11.7); $CoFe_2O_4$ concentration: 2.14 mg L^{-1}; SBA-15, SiO_2, Al_2O_3 supported $CoFe_2O_4$ were made by 2.14 mg L^{-1} $CoFe_2O_4$ and 8 mg L^{-1} SBA-15, 20 mg L^{-1} SiO_2, and 20 mg L^{-1} Al_2O_3, respectively.