Supplementary Information

for

Facile synthesis of Fe_3O_4/MIL-101(Fe) composite with enhanced catalytic performance

Zhongwei Jiang,[a] Fu Qiang Dai, Chengzhi Huang,*[a, b] and Yuanfang Li*[a]

[a]*Key Laboratory of Luminescent and Real-Time Analytical Chemistry (Southwest University), Ministry of Education, College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China. E-mail:liyf@swu.edu.cn, Tel: (+86) 23 68254659, Fax: (+86) 23 68367257.*

[b]*Chongqing Key Laboratory of Biomedical Analysis (Southwest University), Chongqing Science & Technology Commission, College of Pharmaceutical Sciences, Southwest University, Chongqing 400716, China.E-mail: chengzhi@swu.edu.cn.*

Experimental section

1. Synthesis

1.1 Synthesis of MIL-101 (Fe): MIL-101(Fe) was synthesized according to a previous report with a slight modification.[1] Briefly, $FeCl_3·6H_2O$ (1.35 g, 5.0 mmol) and H_2BDC (0.415 g, 2.5 mmol) were dissolved in DMF (30 mL) to form a clear solution. Then, the resulting solution was transferred into a Teflon-lined stainless-steel autoclave and heated at 110 ^oC for 20 h. The resulting brown solid was isolated by centrifugation and washed with DMF and ethanol three times respectively, and then the raw product was purified by washing in hot ethanol (70 ^oC, 3 h), centrifuged, and finally dried overnight at 60 ^oC under vacuum.

1.2 Preparation of magnetic Cys-Fe_3O_4 MNPs: The cysteine (Cys) functionalized Fe_3O_4 MNPs was synthesized by using the reported procedure with some modification.[2] Typically, Equal molar amount of $FeSO_4·7H_2O$ (1.668 g, 6 mmol) and Cys (0.727 g, 6 mmol) were dissolved in 30 mL H_2O, respectively. The resulting solutions were quickly mixed together to form colorless complex under ultrasonic. Then, 48 mL of NaOH (1 M) was rapidly injected into the complex solution accompany with sonication under air at room temperature. For further ultrasonic reaction of 10 minutes, the dark product was isolated by magnetic separation and washed with H_2O for three times, and finally the obtained Cys-Fe_3O_4 MNPs were dried in vacuum freezing drying oven for further use.

1.3 Fabrication of the magnetic hybrid Fe_3O_4/MIL-101(Fe): The Cys-Fe_3O_4 MNPs (20 mg) and MIL-101(Fe) (50 mg) were dispersed in 20 mL H_2O by ultrasonic dispersion method, respectively. Then, 0.5 M K_2CO_3 was used to tune the pH of Cys-Fe_3O_4 MNPs suspension to different value. Finally, the Cys-Fe_3O_4 MNPs suspension was rapidly poured into MIL-101(Fe) suspension under ultrasonication at room temperature. After further ultrasonic reaction for 10 minutes, the brownness product was separated by an external magnet attached to the outside bottom of the vial and washed with H_2O and ethanol two times rspectively. The obtained Fe_3O_4/MIL-101(Fe) was dried in a vacuum oven at 60 °C for further use.

1.4 The catalytic reaction of OPD to 2,3-DPA over Fe_3O_4/MIL-101(Fe): Preparative scale reactions were performed under the following conditions: 50 mg of OPD dissolved in 4 mL H_2O under ultrasonication. The 1.0 M HCl was used to tune the pH of the solution to 3.0. Then, equal volume of H_2O_2 (15%, 150 μL) and Fe_3O_4/MIL-101(Fe) (1mg/mL, 150 μL) was added to the above solution sequentially and diluted to 5 mL. Finally, the mixed solution was stirred at room temperature. The conversion was followed by thin layer chromatography and F-2500 fluorescence spectrophotometer. After 12 h, the catalyst was isolated from the mixture by an external magnet and the insoluble product were dried in vacuum freezing drying oven after alkalizing with $NH_3 \cdot H_2O$. The obtained dark yellow solid was dissolved in methanol and purified by silicagel column chromatography (mobile phase: MeOH–CH_2Cl_2 1: 10) for characterization.

Supporting figures

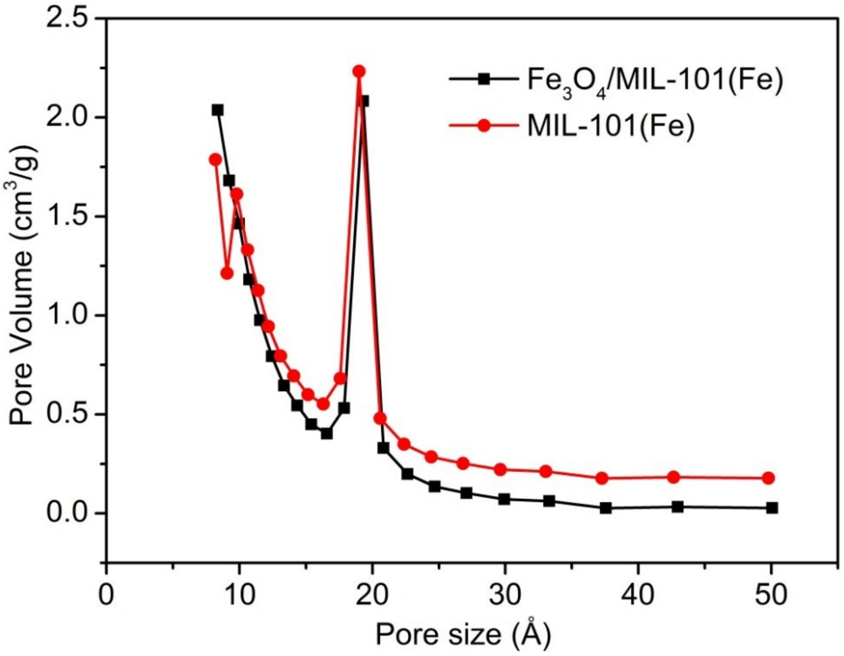


Fig. S1 Pore size distribution profiles of Fe_3O_4/MIL-101(Fe) and MIL-101(Fe).

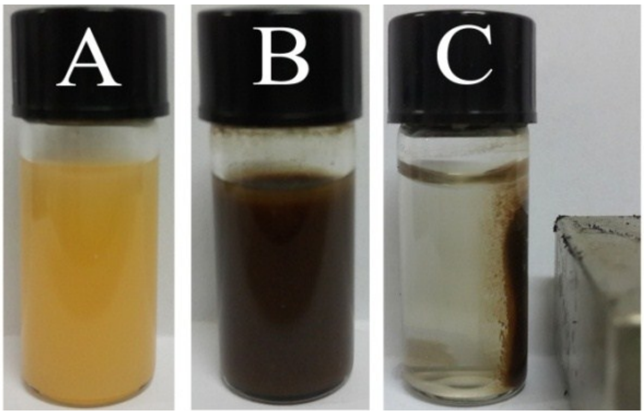


Fig. S2 Photographs for dispersion of MIL-101 (A), Fe_3O_4/MIL-101 (B) and separation of Fe_3O_4/MIL-101 with magnet (C).

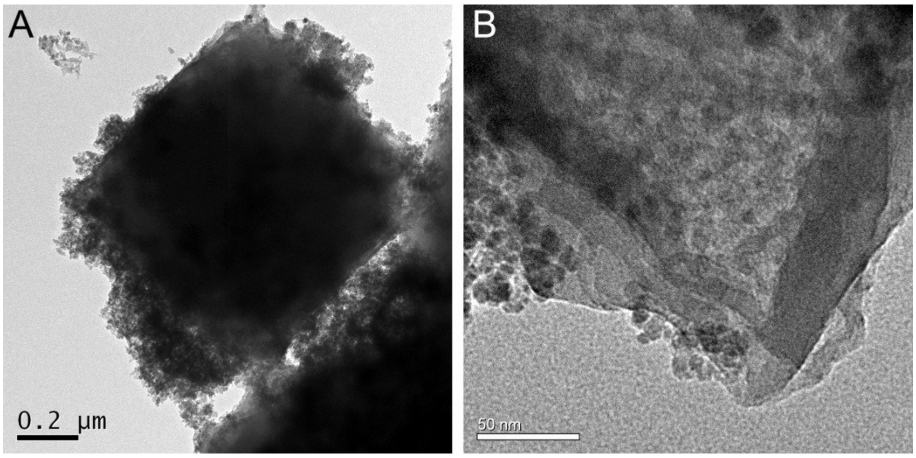


Fig. S3 TEM images of Fe_3O_4/MIL-101(Fe).

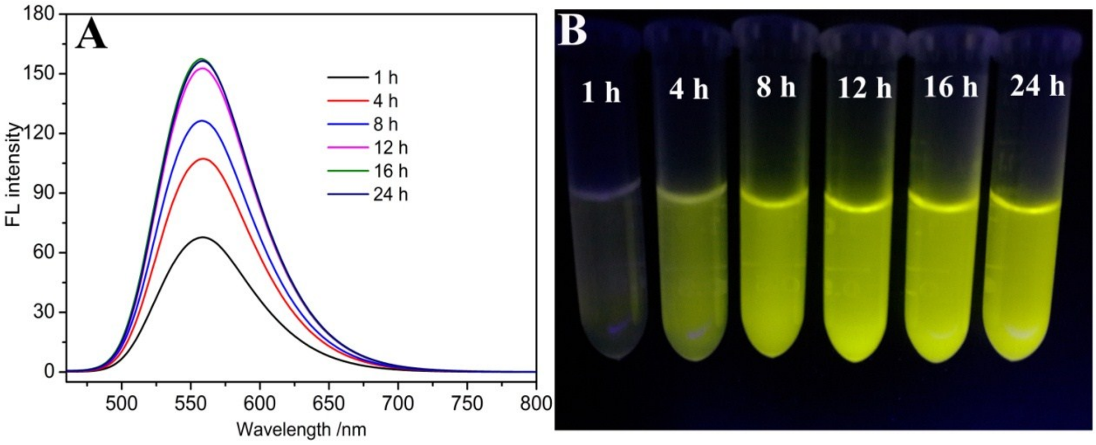
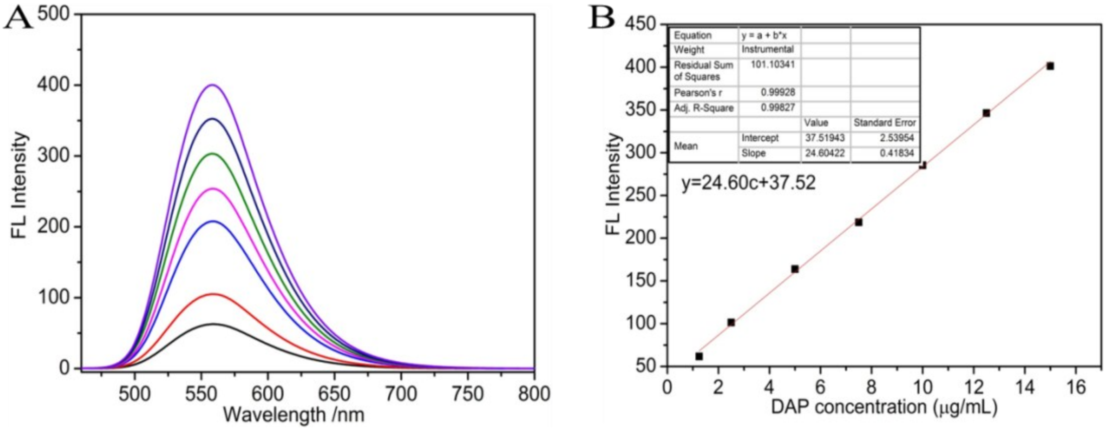


Fig. S4 (A) The changes of 2,3-DPA fluorescence spectra along with the increase of time and (B) the corresponding photograph of fluorescence change of 2,3-DPA under UV 365 nm excitation.



Equation	y = a + b*x		
Weight	Instrumental		
Residual Sum of Squares	101.10341		
Pearson's r	0.99928		
Adj. R-Square	0.99827		
		Value	Standard Error
Mean	Intercept	37.51943	2.53954
	Slope	24.60422	0.41834

Fig. S5 The fluorescence spectra (A) and the standard curve of 2,3-DPA standard (B). (Experimental condition: λ_{ex}=439 nm; λ_{em}=558 nm; voltage=400 V)

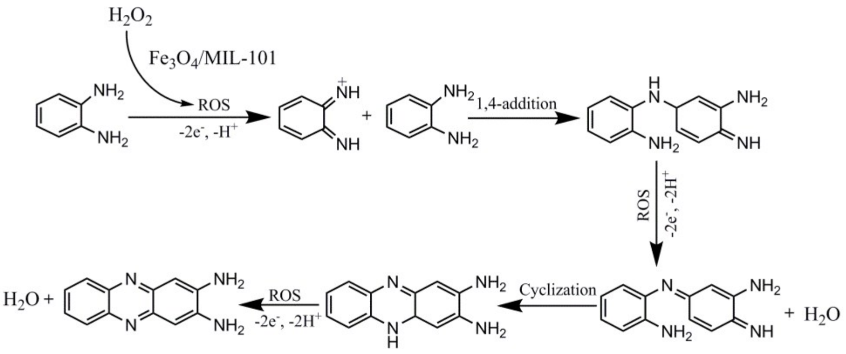


Fig.S6 The possible oxidative pathway for the formation of 2,3-DPA.

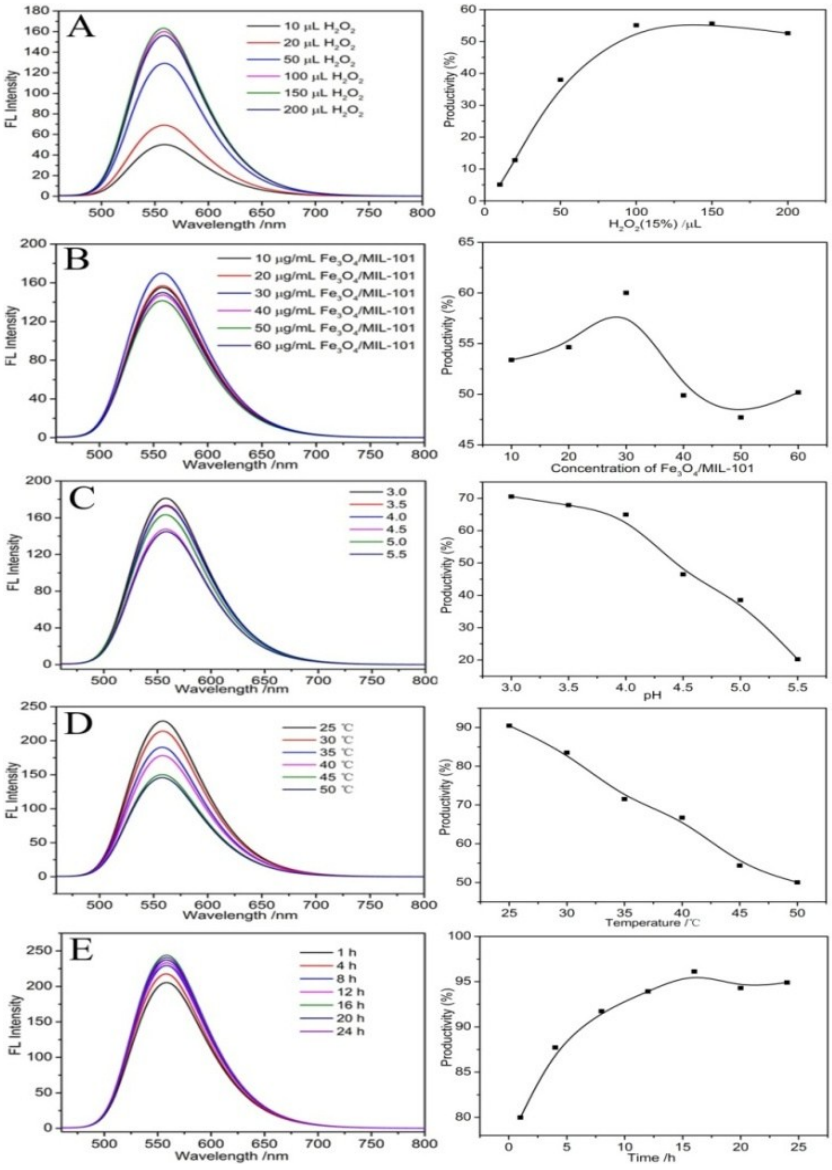


Fig. S7 Optimization of reaction conditions. (A) The concentration of H_2O_2 (15%); (B) concentration of Fe_3O_4/MIL-101(Fe); (C) pH; (D) temperature; (E) reaction time. Left: fluorescence spectrum of product; right: the productivity.

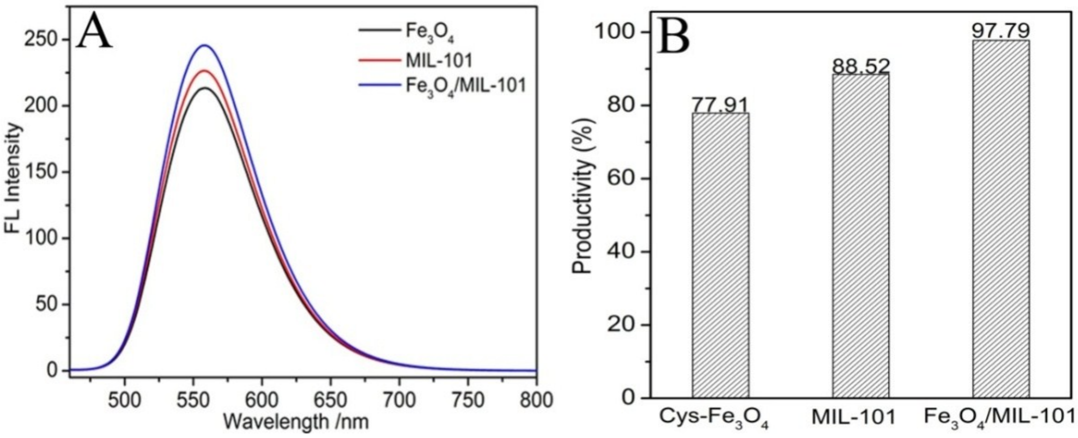


Fig. S8 The comparison of productivity between Fe_3O_4, MIL-101(Fe) and Fe_3O_4/MIL-101(Fe). (A) The fluorescence spectrum of product; (B) the comparison of productivity.

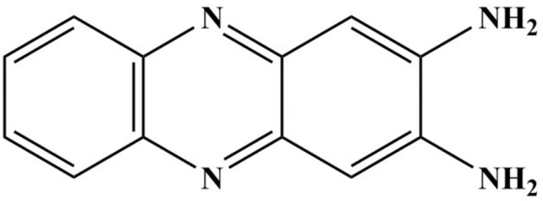


Fig.S9 The structure of 2,3-diaminophenazine.

For the product DPA, the characterization data of FTIR, ^{1}H NMR, ^{13}C NMR and ESI-TOFMS are showed in Fig. S9, Fig. S10, Fig. S11 and Fig. S12 respectively. Typically, FTIR (KBr) ν(cm^{-1}): 3433, 3309, 3174, 1643, 1492, 1469, 1411,1338, 1226, 1138, 759; ^{1}HNMR (600MHz, DMSO-d_6): δ (ppm) =7.91 (dd, J = 6.5, 3.4 Hz, 2H), 7.54 (dd, J = 6.5, 3.4 Hz, 2H), 6.94 (s, 2H), 6.26 (s, 4H).； ^{13}CNMR (DMSO-d_6): δ (ppm) = 144.04 (s), 142.04 (s), 140.29 (s), 127.84 (s), 126.39 (s) and 102.25 (s); ESI-TOFMS: m/z = 211.1 $[M + H]^+$.

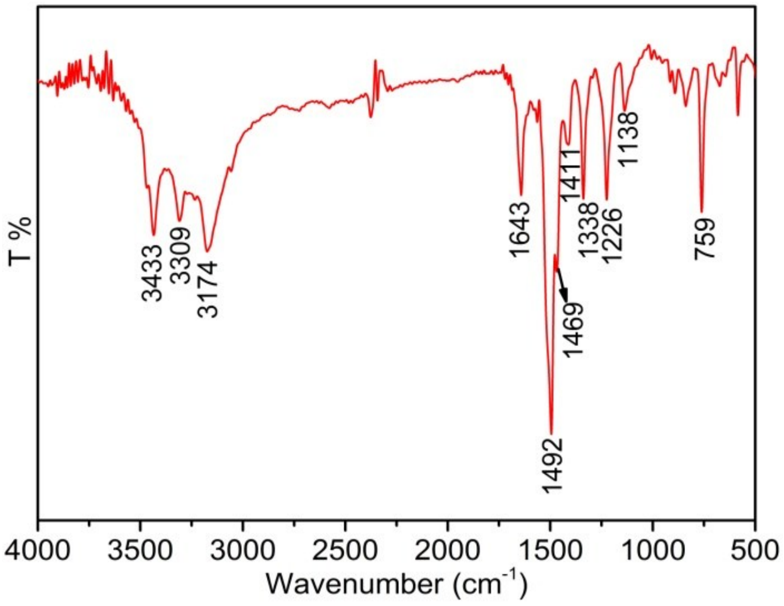


Fig. S10 FTIR spectra of 2,3-diaminophenazine

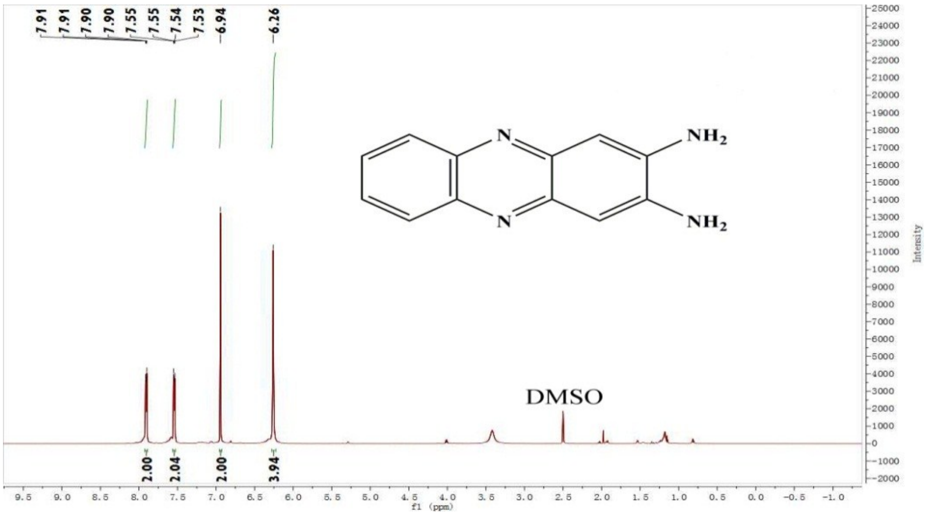


Fig. S11 The ^{1}HNMR spectra of 2,3-diaminophenazine

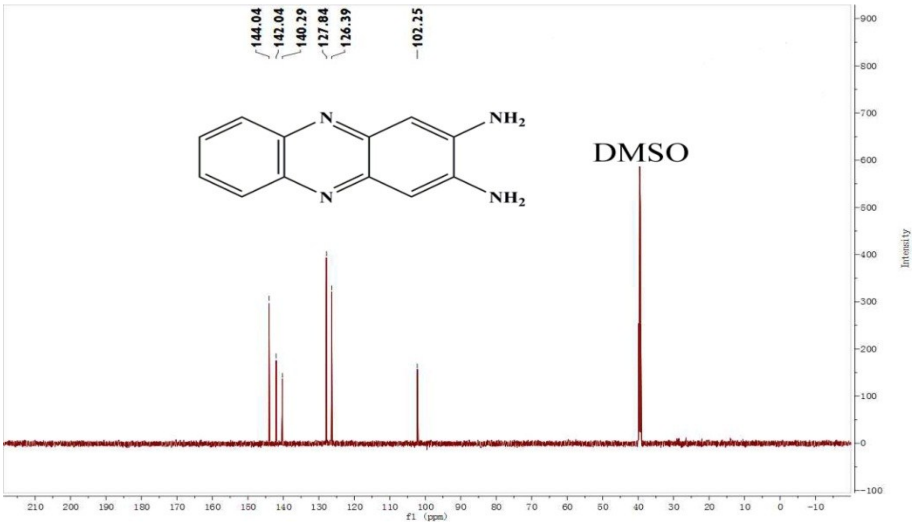


Fig. S12 The ^{13}CNMR spectra of 2,3-diaminophenazine

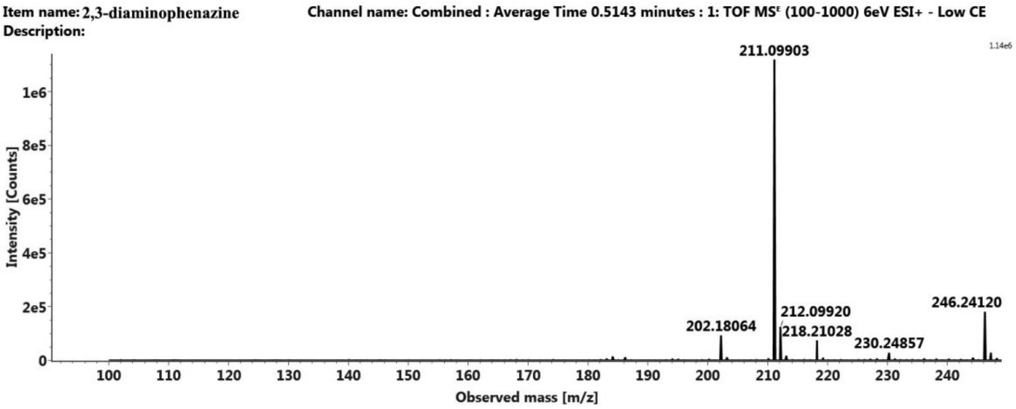


Fig. S13 The ESI-TOFMS spectra of 2,3-diaminophenazine

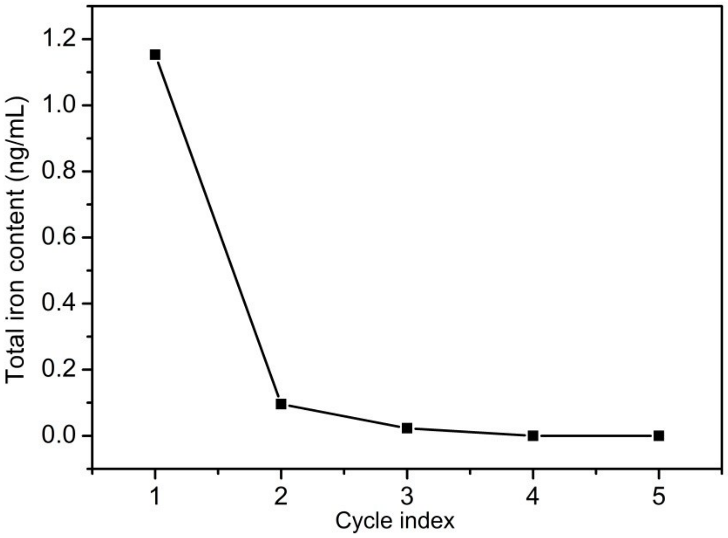


Fig. S14 The leaching test during the recycle using.

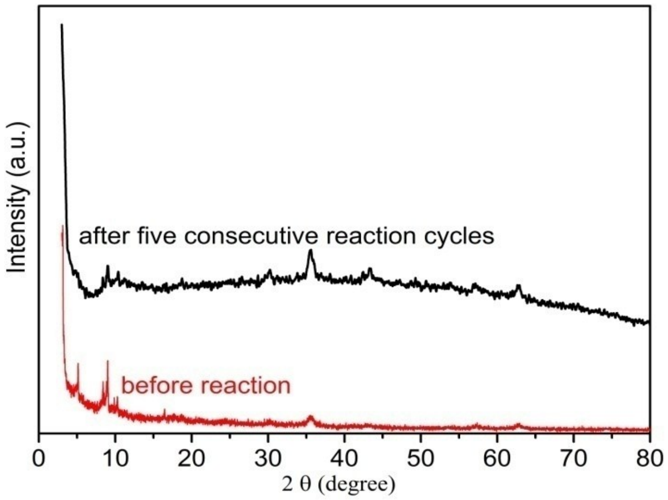


Fig. S15 PXRD patterns of Fe_3O_4/MIL-101(Fe) before and after five consecutive reaction cycles.

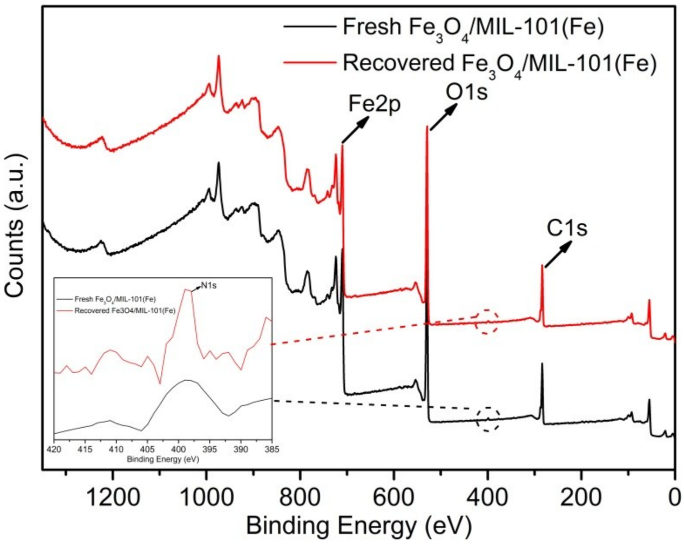


Fig.S16 XPS survey spectra of Fe_3O_4/MIL-101(Fe).

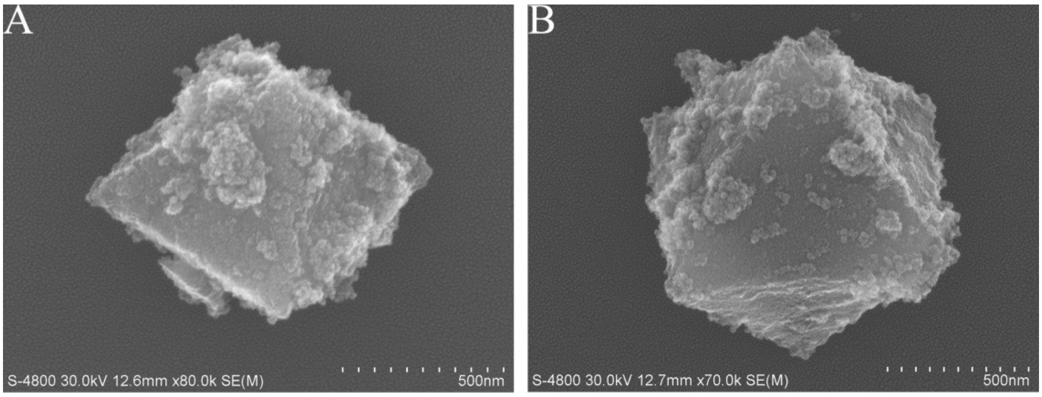


Fig. S17 The morphology of Fe_3O_4/MIL-101(Fe) before (A) and after five consecutive reaction cycles (B).

Table S1 Comparison of the catalytic efficiency of the as-prepared Fe_3O_4/MIL-101(Fe) and other existing catalyst

Catalysts	Catalytic efficiency (%)	Ref.
HRP	42.00	3
CotA-laccase	66.00	4
Copper chloride	23.04	5
Copper(II) complexes	16.67	6
Fe_3O_4/MIL-101(Fe)	97.79	Present work

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