Supplementary Information

for

Facile synthesis of Fe₃O₄/MIL-101(Fe) composite with enhanced catalytic performance

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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, FeCl₃·6H₂O (1.35 g, 5.0 mmol) and H₂BDC (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 °C 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 °C, 3 h), centrifuged, and finally dried overnight at 60 °C under vacuum.

1.2 Preparation of magnetic Cys-Fe₃O₄ MNPs: The cysteine (Cys) functionalized Fe₃O₄ MNPs was synthesized by using the reported procedure with some modification.2 Typically, Equal molar amount of FeSO₄·7H₂O (1.668 g, 6 mmol)
and Cys (0.727 g, 6 mmol) were dissolved in 30 mL H₂O, 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 H₂O for three times, and finally the obtained Cys-Fe₃O₄ MNPs were dried in vacuum freezing drying oven for further use.

1.3 Fabrication of the magnetic hybrid Fe₃O₄/MIL-101(Fe): The Cys-Fe₃O₄ MNPs (20 mg) and MIL-101(Fe) (50 mg) were dispersed in 20 mL H₂O by ultrasonic dispersion method, respectively. Then, 0.5 M K₂CO₃ was used to tune the pH of Cys-Fe₃O₄ MNPs suspension to different value. Finally, the Cys-Fe₃O₄ 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 H₂O and ethanol two times respectively. The obtained Fe₃O₄/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 Fe₃O₄/MIL-101(Fe):
Preparative scale reactions were performed under the following conditions: 50 mg of OPD dissolved in 4 mL H₂O under ultrasonication. The 1.0 M HCl was used to tune the pH of the solution to 3.0. Then, equal volume of H₂O₂ (15%, 150 µL) and Fe₃O₄/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 NH₃·H₂O. The obtained dark yellow solid was dissolved in methanol and purified by silicagel column chromatography (mobile phase: MeOH–CH₂Cl₂ 1: 10) for characterization.
Supporting figures

Fig. S1 Pore size distribution profiles of Fe₃O₄/MIL-101(Fe) and MIL-101(Fe).

Fig. S2 Photographs for dispersion of MIL-101 (A), Fe₃O₄/MIL-101 (B) and separation of Fe₃O₄/MIL-101 with magnet (C).
Fig. S3 TEM images of Fe₃O₄/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.

Fig. S5 The fluorescence spectra (A) and the standard curve of 2,3-DPA standard (B). (Experimental condition: λₑₓ=439 nm; λₑₘ=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 H₂O₂ (15%); (B) concentration of Fe₃O₄/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 Fe₃O₄, MIL-101(Fe) and Fe₃O₄/MIL-101(Fe). (A) The fluorescence spectrum of product; (B) the comparison of productivity.

![Fig. S8 fluorine spectrum and comparison of productivity](image)

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

For the product DPA, the characterization data of FTIR, ¹H NMR, ¹³C 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; ¹H NMR (600MHz, DMSO-d₆): 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); ¹³C NMR (DMSO-d₆): 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 Fe₃O₄/MIL-101(Fe) before and after five consecutive reaction cycles.

Fig. S16 XPS survey spectra of Fe₃O₄/MIL-101(Fe).

Fig. S17 The morphology of Fe₃O₄/MIL-101(Fe) before (A) and after five consecutive reaction cycles (B).
Table S1 Comparison of the catalytic efficiency of the as-prepared Fe₃O₄/MIL-101(Fe) and other existing catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Catalytic efficiency (%)</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>HRP</td>
<td>42.00</td>
<td>3</td>
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<tr>
<td>CotA-laccase</td>
<td>66.00</td>
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<tr>
<td>Copper chloride</td>
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<td>5</td>
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<tr>
<td>Copper(II) complexes</td>
<td>16.67</td>
<td>6</td>
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<tr>
<td>Fe₃O₄/MIL-101(Fe)</td>
<td>97.79</td>
<td>Present work</td>
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