Electronic Supplementary Information (ESI)

Fe-pyridinedicarboxylate based coordination polymer nanorods as heterogeneous Fenton catalyst for pollutant degradation

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Experimental details

Materials and methods
All the chemicals were obtained commercially and used as received without further purification. Scanning electron microscope (SEM) images were taken with a JEOL JSM-7500F scanning electron microscope. \( \text{N}_2 \) adsorption-desorption isotherm measurement was operated on a V-Sorb 2800P surface area and pore size analyzer. The powder X-ray diffraction (PXRD) spectra were collected on a Rigaku D/Max-2500 diffractometer with Cu K\( \alpha \) radiation (\( \lambda = 0.15406 \) nm), samples were scanned at 60 kV and 300 mA. Fourier transform infrared spectroscopy (FT-IR) was measured by a Nicolet Avatar 370 Fourier transform infrared spectrometer with nujol mull method. Elemental analysis (C, H, and N) was carried out on a Perkin-Elmer 240C analyzer. Thermogravimetric analysis (TGA) was performed with a Rigaku standard TG-DTA analyzer from ambient temperature to 700 °C with a heating rate of 10 °C min\(^{-1}\) in the air, and an empty Al\(_2\)O\(_3\) crucible was used as the reference. The concentrations of substrate and formed intermediates in the solution were analyzed by HPLC method (Agilent LC 1200). Electron spin resonance (ESR) spectra were obtained using a Brucker model EPR 300E spectrometer. UV-Vis spectroscopy was performed with a Shimadzu UV-2450 spectrophotometer.

Synthesis of Fe-bpydc
0.0835 g (0.5 mmol) of 2,5-pyridinedicarboxylic acid was dissolved in 6 mL of DMF. After the addition of 6 mL aqueous solution of FeSO\(_4\) (0.5 mmol), the mixture was transferred into a 25 mL Teflon-lined stainless steel autoclave and heated at 120 °C for 12 h. The formed precipitate of Fe-bpydc was separated by filtration, washed by water and ethanol in sequence, and dried at 60 °C for 6 h.

Catalytic degradation experiments
In a typical procedure, 2 mg of Fe-pydc was dispersed in 200 mL aqueous solution of organic substrates, and stirred for 2 h to reach the adsorption-desorption equilibrium. Then 1.5 mM of H\(_2\)O\(_2\) was added to start the reaction. After reacted for a given time, ca. 1 mL aliquot was collected and filtered to remove the catalyst. The concentrations of colorless substrates in the filtrates were determined with HPLC method, while the degradations of organic dyes were quantified with UV-Vis spectra at the absorption maximum. The concentration of H\(_2\)O\(_2\) was measured by the spectrophotometric DPD method.\(^1\)
Fig. S1  $N_2$ adsorption–desorption isotherms of (a) as-prepared and (b) used Fe-pydc samples.

Fig. S2  PXRD pattern of the as-prepared Fe-pydc sample.

Fig. S3  Framework structure of $[Fe_2(pydc)_2(H_2O)_6]^2$.2
Fig. S4 FT-IR spectrum of the as-prepared Fe-pydc sample.

Fig. S5 XPS spectrum of the as-prepared and used Fe-pydc sample.

Fig. S6 TGA curve of the as-prepared Fe-pydc sample.
Fig. S7  Degradation kinetics of phenol with Fe-pydc/H\textsubscript{2}O\textsubscript{2}, FeO/H\textsubscript{2}O\textsubscript{2} and Fe(II)/H\textsubscript{2}O\textsubscript{2} conditions. 17.6 \(\mu\)mol L\(^{-1}\) (0.01 g L\(^{-1}\)) Fe-pydc, 35.2\(\mu\)mol L\(^{-1}\) (0.0025 g L\(^{-1}\)) FeO or 35.2\(\mu\)mol L\(^{-1}\) FeSO\(_4\) (0.01 g L\(^{-1}\)) was used as catalyst, \(c\text{phenol}^0 = 0.25\) mM, \(c\text{H}_2\text{O}_2^0 = 1.5\) mM, 200 mL H\(_2\)O.

Fig. S8  SEM image of the Fe-pydc catalyst after the degradation of phenol.

Fig. S9  Typical HPLC chromatogram of the reacted solution of phenol. 0.0025 g L\(^{-1}\) Fe-pydc, \(c\text{phenol}^0 = 0.5\) mM, \(c\text{H}_2\text{O}_2^0 = 1.5\) mM, 200 mL H\(_2\)O.
**Fig. S10**  Concentration change of intermediates during the degradation of phenol. 0.0025 g L\(^{-1}\) Fe-pydc, \(c_{\text{phenol}}^0 = 0.5\) mM, \(c_{\text{H}_2\text{O}_2}^0 = 1.5\) mM, 200 mL H\(_2\)O.

**Fig. S11**  Consumption rates of phenol under the catalysis of 0.0025 g L\(^{-1}\) Fe-pydc. (a) \(c_{\text{phenol}}^0 = 0.25\) mM. (b) \(c_{\text{H}_2\text{O}_2}^0 = 1.5\) mM.

**Fig. S12**  Degradation kinetics of (a) \(p\)-chlorophenol and (b) benzoic acid in the catalytic oxidation system of Fe-pydc. 0.01 g L\(^{-1}\) Fe-pydc, 0.005g L\(^{-1}\) substrates, \(c_{\text{H}_2\text{O}_2}^0 = 1.5\) mM, 200 mL H\(_2\)O.
Fig. S13  Degradation kinetics of (a) methylene blue, (b) methyl orange and (c) rhodamin B in the catalytic oxidation system of Fe-pydc. 0.01 g L\(^{-1}\) Fe-pydc, 0.005g L\(^{-1}\) substrates, \(c_{\text{H}_2\text{O}_2}\) = 1.5 mM, 200 mL H\(_2\)O. Inset: the change of absorption spectrum of the reacted solution.

References