



# Iron terephthalate metal–organic framework: Revealing the effective activation of hydrogen peroxide for the degradation of organic dye under visible light irradiation



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## ABSTRACT

Metal–organic frameworks (MOFs), a new class of porous crystalline materials, have attracted great interest as a promising candidate for sustainable energy and environmental remediation. In this study, we demonstrate that an iron terephthalate metal–organic framework MIL-53(Fe) synthesized by a facile solvothermal reaction was capable of activating hydrogen peroxide ( $H_2O_2$ ) to achieve high efficiency in photocatalytic process. It could completely decompose the  $10\text{ mg L}^{-1}$  Rhodamine B (RhB) in the presence of a certain amount of  $H_2O_2$  under visible light irradiation within 50 min. The catalytic activities were found to be strongly affected by the various operating parameters, such as solution pH, initial dye concentration, and  $H_2O_2$  dosage. The activation effects of MIL-53(Fe) were investigated through the detection of hydroxyl radicals ( $\cdot OH$ ) and transient photocurrent responses, which revealed that the  $H_2O_2$  behaved in two ways during the catalytic process: (i) it could be catalytically decomposed by MIL(Fe)-53 to produce  $\cdot OH$  radicals through the Fenton-like reaction; (ii) it could capture the photogenerated electrons in the conduction band of excited MIL-53(Fe) to form  $\cdot OH$  radicals under visible light irradiation. The ability of such iron-based MOFs to activate  $H_2O_2$  may enable rational design of advanced MOF-based catalysts for environmental remediation.

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## 1. Introduction

Increasing global contamination of water body and deterioration of water quality has become a serious issue facing humanity in the current situation. The ever-increasing demand for clean water environment has triggered intense research on the advanced technology for water treatment. Among versatile physical, chemical, and biological technologies in pollution control, the advanced oxidation processes (AOPs), including Fenton reaction, photocatalysis, sonolysis, ozonation and their combination, are of great practical importance due to their high efficiency, simplicity, good reproducibility, and easy handling. AOPs generally involve an in situ generation of highly reactive and nonselective chemical oxidants such as hydroxyl radicals ( $\cdot OH$ ) to degrade the persistent and non-biodegradable organic substances [1,2]. In particular, the utilization of an environmentally benign oxidant, hydrogen peroxide ( $H_2O_2$ ), to produce  $\cdot OH$  has attracted considerable attention. Actually,  $H_2O_2$  could decompose easily to  $\cdot OH$  upon activation by transition metal ions (e.g.,  $Fe^{2+}$ ,  $Fe^{3+}$ , and  $Cr^{6+}$ ) [3,4], inorganic bicarbonate ions [5,6],

UV light irradiation and ultrasound irradiation. However, most of these approaches require rigorous operating pH range, long run times and increased energy consumption. Therefore, great research effort has been devoted to develop a heterogeneous solid catalyst system activating  $H_2O_2$  to overcome the critical drawbacks of above homogeneous catalytic process. For example, iron-based heterogeneous Fenton-like catalysts have been explored as activation catalysts for  $H_2O_2$ , including  $Fe_3O_4$  [7],  $\alpha\text{-FeOOH}$  [8],  $FeVO_4$  [9],  $BiFeO_3$  [10], Fe alginate [11] and Fe-ZSM5 zeolite [12], to efficiently degrade organic dyes in aqueous solution. Meanwhile, recent studies have also shown that  $H_2O_2$  could be activated by the semiconductor photocatalysts such as  $TiO_2$ ,  $BiVO_4$  [13],  $g\text{-C}_3\text{N}_4$  [14],  $WO_3$  [15],  $K_3PW_{12}O_{40}$  [16], and  $ZnFe_2O_4$  [17], facilitating to enhance the photocatalytic efficiency under visible light irradiation. Apparently, design and fabrication of the effective heterogeneous catalysts for  $H_2O_2$  activation is a key issue to realize the desirable activity and long-term stability.

Metal–organic frameworks (MOFs) have emerged as an interesting class of multifunctional inorganic–organic hybrid porous crystalline materials, where metal ions or clusters are linked to organic linkers forming a three-dimensional well-defined structure, owing to their promising applications in gas storage, separation, catalysis, sensors and drug delivery [18–21]. Importantly,

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recent progress has shown that MOFs show an attractive semi-conducting behavior that integrates different molecular functional components to achieve light harvesting and to photocatalytically drive various chemically useful reaction [22–24]. In contrast to the conventional semiconductor photocatalytic systems, photoactive MOF systems have advantages in solar harnessing more efficiently, as their structural features of tunable active sites (i.e., metal-oxo clusters and organic linkers), desirable porosity and high surface area allow not only for rational design and fabrication of the photocatalytic system at the molecular level, but also for fast transport and good accommodation of guest molecules. To this end, MOFs could serve as an ideal choice for light harvesting to achieve photocatalytic degradation of organic pollutions. For example, A MOF-5 behaves as a semiconductor upon light excitation for the generation of charge carriers (electrons and holes), which was able to photocatalytically degrade phenol in aqueous solutions [25]. A Cu-doped ZIF-67 has been used as a visible-light-driven photocatalyst for the degradation of methyl orange [24]. Chen et al. reported that a doubly interpenetrated semiconducting MOF UTSA-38 with a band gap of 2.85 eV exhibited photocatalytic activity for the degradation of methyl orange in aqueous solution [26]. Despite the great progress achieved so far, it is still essential to exploit high performance visible-light-responsive MOF-based photocatalysts.

Herein, we demonstrate the capability of an iron-based metal–organic framework MIL-53(Fe) for the activation of hydrogen peroxide ( $H_2O_2$ ) to achieve high efficiency in visible light photocatalytic process. The photocatalytic rates of RhB degradation over MIL-53(Fe) were accelerate evidently with the assistance of  $H_2O_2$ . The activation mechanism of MIL-53(Fe) was investigated and proposed on the basis of experiment results of the detection of hydroxyl radicals and transient photocurrent responses, which confirm the enhanced photocatalytic activity could be arisen from the cooperative effects by combination of MIL-53(Fe) and  $H_2O_2$  under visible light irradiation.

## 2. Experimental

### 2.1. Materials

$FeCl_3 \cdot 6H_2O$ , terephthalic acid (1,4-BDC), dimethylformamide (DMF), Rhodamine B (RhB),  $H_2O_2$  (30%, v/v), HCl and NaOH were purchased from Kelong Chemical Reagents Company (Chengdu, China) and used without further purification. All chemicals used in this study were of commercially available analytical grade.

### 2.2. Preparation of metal–organic framework MIL-53(Fe)

Metal–organic framework MIL-53(Fe) was prepared by a mild solvothermal process [27]. In a typical procedure, 1 mmol of  $FeCl_3 \cdot 6H_2O$  and 1 mmol of 1,4-BDC were added slowly into 5 mL of DMF solution. The mixture was stirred for 10 min at room temperature, and then transferred into a Teflon-lined stainless steel autoclave with a volume capacity of 20 mL and heated at 150 °C for 2 h. After the heat treatment, the autoclave is allowed to cool naturally to room temperature, and the products are collected by centrifugation at 6000 rpm for 2 min. To remove the solvent, the obtained yellow powder was suspended into a 200 mL of distilled water overnight, and then centrifuged in water and dried in vacuum at 60 °C for 24 h.

### 2.3. Characterization

The powder X-ray diffraction (PXRD) measurements were recorded on a Rigaku Dmax/Ultima IV diffractometer with monochromatized Cu  $K\alpha$  radiation ( $\lambda = 0.15418$  nm). The morphology was observed with a JEOL JSM-6510LV scanning electron

microscope (SEM). The elemental composition of the samples were characterized by energy-dispersive X-ray spectroscopy (EDS, Oxford instruments X-Max). The Fourier transform infrared (FTIR) spectroscopy was recorded on Nicolet 6700 FTIR Spectrometric Analyzer using KBr pellets. UV–vis diffused reflectance spectra of the samples were obtained for the dry-pressed film samples using a UV–vis spectrophotometer (UV-3600, Shimadzu, Japan).  $BaSO_4$  was used as a reflectance standard in a UV–vis diffuse reflectance experiment. The Brunauer–Emmett–Teller (BET) surface area and porous structure were measured using an ASAP 2020 V3.01 H apparatus (Micromeritics Instrument Corp., USA). After the samples were degassed in vacuum at 120 °C for 6 h, the nitrogen adsorption and desorption isotherms were measured at 77 K.

### 2.4. Degradation experiments

The visible light photocatalytic degradation of RhB in the presence of  $H_2O_2$  over MIL-53(Fe) was carried out in a cylindrical Pyrex vessel reactor. Typically, 0.01 g MIL-53(Fe) sample was added into 25 mL of RhB in a 100 mL cylindrical Pyrex vessel. Afterwards, suspension was mechanically stirred in the dark for 30 min to establish the adsorption/desorption equilibrium, followed by the addition of a known concentration of  $H_2O_2$  to the mixture solution. The suspension was then illuminated by a 500 W halogen tungsten lamp through a UV-cutoff filter (420 nm). At predetermined time intervals, the suspension were extracted at different time intervals and then centrifuged to get the supernatant for analysis.

### 2.5. Analytical methods

The concentration of RhB left in the supernatant solution was determined by using a Shimadzu UV2550 UV–vis spectrophotometer at its maximum absorption wavelength of 554 nm. The pH of RhB solution was adjusted by adding aqueous solutions of 0.1 mol L<sup>-1</sup> HCl or 0.1 mol L<sup>-1</sup> NaOH, and determined by using a PHS-3C pH meter (Rex Instrument Factory, Shanghai, China). The formation of hydroxyl radicals ( $\cdot OH$ ) mediated by MIL-53(Fe) catalysts in the presence of  $H_2O_2$  was detected by fluorescence method using terephthalic acid as a probe molecule [28]. The experimental procedures were similar to those used in the measurement of above catalytic experiments in the presence of  $H_2O_2$  under visible light irradiation except that the aqueous solution of RhB was replaced by an aqueous solution of 0.5 mM terephthalic acid and 2 mM NaOH. The visible light irradiation was continuous and sampling was performed every 5 min for analysis with a RF-5301PC Shimadzu fluorescence spectrophotometer at 315 nm of excitation wavelength.

### 2.6. Electrochemical measurements

An electrochemical work station (CHI660D Instruments) connected to a computer was used in our electrochemical experiment. The electrodes were prepared according to Zhang's method [29]. For the preparation of the MOF electrodes, the MIL-53(Fe) were dispersed in chitosan solution to form a 10 mg mL<sup>-1</sup> solution and ultrasonicated for 5 min, 0.3 mL of colloidal solution was dropped on the pretreated ITO surface and allowed to dry under vacuum conditions for 24 h at room temperature. The photocurrents were measured by an electrochemical analyzer in a standard three-electrode system with the MIL-53(Fe) as the working electrodes, a Pt foil as the counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. A 500 W Xe arc lamp with a UV-cutoff filter (420 nm) was utilized as a light source. A 0.5 M  $Na_2SO_4$  aqueous solution was used as the electrolyte. The Mott–Schottky measurements were carried out with impedance-potential model to evaluate the band positions of the MIL-53(Fe) catalyst.

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