



MIL-68(Fe) as an efficient visible-light-driven photocatalyst for the treatment of a simulated waste-water contain Cr(VI) and Malachite Green



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ABSTRACT

A highly effective Iron Metal-Organic Framework photocatalyst (MIL-68(Fe)) has been successfully prepared via a facile solvothermal method under acidic condition. The UV–vis diffuse reflectance spectrum reveals that the absorption edge of MIL-68(Fe) is 440 nm. The flat-band potential of MIL-68(Fe) is -0.6 V vs. NHE at pH = 6.8, which is more negative than the redox potential of Cr(VI)/Cr(III) ($+0.51$ V, pH = 6.8). Consequently, it is thermodynamically permissible for the transformation of photogenerated electrons to the Cr(VI) to produce Cr(III). Moreover, MIL-68(Fe) could perform as an efficient photocatalyst towards the reduction of Cr(VI) aqueous with a wide pH range. After 5 min of visible light illumination ($\lambda > 420$ nm), almost 100% Cr(VI) can convert to Cr(III) with $(\text{NH}_4)_2\text{C}_2\text{O}_4$ as a scavenger (pH = 3), which is also higher than that of N-doped TiO₂ (50%) and ZnO (7.6%) under identical conditions. Furthermore, MIL-68(Fe) is proved to perform as a highly efficient photocatalyst for removal of different aqueous contaminant with malachite green (MG) as a scavenger. Finally, a possible reaction mechanism has also been investigated in detail.

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1. Introduction

Hexavalent chromium species (Cr(VI)) are highly toxic substances have been regarded as carcinogens, mutagens and teratogens in biological systems. They mainly arise from industrial waste-water, for instance, tanning, metallurgy, plating and metal finishing [1]. The researches have shown that excessive concentrations of Cr(VI) will have lethal effects to aquatic life and the levels of chromium in water should be reduced to 0.1 ppm [2]. Consequently, the removing of Cr(VI) from wastewater is an urgent need. To date, many techniques have been adopted for Cr(VI) removing, such as reduction, precipitation, ion exchange, reverse osmosis and photocatalytic reduction [1,3,4]. Because of its clean and environmentally friendly and relatively effective, photocatalytic reduction technology has attracted great interest. It is well-known that TiO₂-based or ZnO-based photocatalysts could exhibit considerable activity for removing Cr(VI) [5,6]. Unfortunately, these materials show a low utilization rate of solar energy in the photocatalytic reaction. There-

fore, it is necessary to explore efficient novel visible-light-driven photocatalysts.

Metal-organic frameworks (MOFs) have been aroused great attention in the past decade, because of their spatial structure, large surface area and pore volume [7,8]. Up to now, MOFs have been successfully applied in gas storage, adsorption, separation, catalysis and drug delivery [9–13]. Since the first report on photocatalytic activity in MOF-5, more and more MOFs such as Ni-MOF [14], MIL-101(Cr) [15], NH₂-MIL-68(In) [11] and NH₂-UiO-66(Zr) [16] can behave as pseudo-semiconductors. Among MOFs materials, Fe based Metal-organic frameworks material (Fe-MOFs) have becoming a promising photocatalysts owing to their high chemical stability, non-toxic, low cost and photosensitivity [17]. In our previous works, MIL-53(Fe) and MIL-100(Fe) were found to show good photocatalytic performances under visible light [17–19]. As one of Fe based metal-organic framework, Fe-benzenedicarboxylate (MIL-68(Fe)) was first reported by Gérard Férey group, which consists of chains of corner-sharing Fe(OH)₂O₄ octahedral connected through a BDC (terephthalic acid) linker [20]. Compared with other Fe-MOFs, the reports on MIL-68(Fe) for photocatalytic applications are rather scarce [21,22]. Especially, utilization of MIL-68(Fe) for photocatalytic reduction under visible light has remained unavailable so far.

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Herein, we have reported photocatalytic performance of MIL-68(Fe) for the reduction of Cr(VI) to Cr(III) under visible light irradiation. Meanwhile, the factors that affect the Cr(VI) reduction, such as the pH value of the reaction solution has also been investigated in detail. Fortunately, MIL-68(Fe) could also perform as a difunctional photocatalyst for the treatment of different types of water contaminants (the mixed of dyes and Cr(VI)), simultaneously. Finally, a possible reaction mechanism of photocatalytic reduction of Cr(VI) and degradation of dye (MG) solutions through MIL-68(Fe) have also been investigated in detail.

2. Experimental

2.1. Materials and reagents

Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was supplied by Aladdin Reagent Co., Ltd. 1,4-benzenedicarboxylic acid (H_2BDC) was obtained from Alfa Aesar China Co., Ltd., potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), *N,N*-Dimethylformamide (DMF), hydrofluoric acid (HF, 49%), Malachite Green (MG), ZnO and ammonium oxalate ($(\text{NH}_4)_2\text{C}_2\text{O}_4$) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All materials were used as received without further purification. N-TiO_2 was prepared by laboratory.

2.2. Synthesis of MIL-68(Fe) samples

MIL-68(Fe) was obtained according to the strategy that reported in previous [20,21]. A molar amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and H_2BDC (molar ratio = 1:2) were mixed with 12 mL DMF in a Teflon-lined autoclave, then 120 μL HF (5 mmol) and 120 μL HCl (1 mmol) were added, followed stirring for another 30 min to blend completely. After that, the Teflon-lined was heated at 100 °C for 120 h. The products were left cool at room temperature, collected by centrifugation and washed with deionized water and acetone several times to eliminate the DMF molecules in the pores. Finally, the recovered solid was dried at 100 °C vacuum oven for 24 h.

2.3. Characterizations

The X-ray diffraction (XRD) patterns of the samples were carried on a Bruker D8 Advance X-ray diffractometer operated at 40 kV and 40 mA with Ni-filtered Cu K α irradiation. The data were recorded in the 2θ ranging from 3° to 50° with a step width of 0.05°. UV-vis diffuse reflectance spectra (UV-vis DRS) were obtained by a Cary 500 UV-vis-NIR spectrophotometer in which BaSO_4 powder was used as the internal standard to obtain the optical properties of the samples over a wavelength range of 200–800 nm. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a PHI Quantum 2000 XPS system equipped with a monochromatic Al K α X-ray source to obtain the surface elemental composition of the sample. The Fourier transformed infrared spectra (FTIR) was carried out on a Nicolet Nexus 670 Fourier transform infrared spectrometer. The Mott-Schottky analysis was performed at a Zenuium electrochemical workstation. The electrochemical measurements were performed in a conventional three electrode cell, Ag/AgCl electrode was used as the reference electrode and a Pt plate was used as the counter electrode. The working electrode was prepared on fluorine-doped tin oxide (FTO) glass, which was previously cleaned by ethanol and deionized water. The slurry was obtained from 5 mg photocatalyst which ultrasonicated in 0.5 mL of *N,N*-dimethylformamide, then dip-coated on the surface of the FTO glass, whose side part was previously protected using Scotch tape. After dried overnight under nature conditions, a copper wire was connected to the side part of the FTO glass using conductive tape. The working electrodes were immersed in a 0.2 M Na_2SO_4

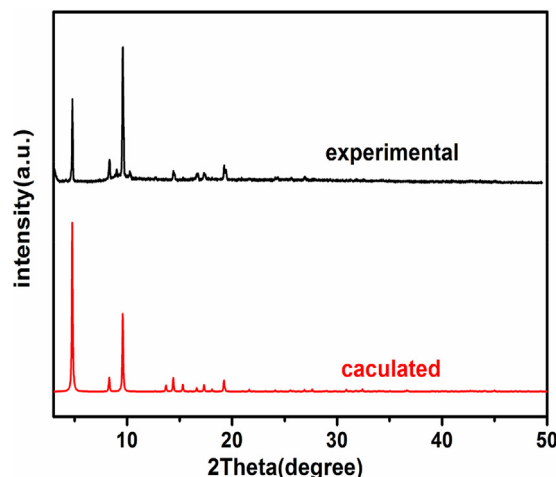


Fig. 1. XRD patterns of the as-prepared and calculated MIL-68(Fe).

(pH = 6.8) aqueous solution without any additive for 30 s before measurement.

2.4. Evaluation of photocatalytic activity

The photocatalytic activity of the prepared samples was evaluated by reduction of aqueous Cr(VI) under visible irradiation. In a typical reaction, 10 mg photocatalysts and 5 mg $(\text{NH}_4)_2\text{C}_2\text{O}_4$ were added into 40 mL of 20 ppm Cr(VI) solution in a 100 mL quartz vial. The pH values of solutions were adjusted with H_2SO_4 (2 mol L $^{-1}$). Before illumination reaction started, the suspension was stirred in the dark for 40 min to establish the adsorption–desorption equilibrium between the samples and the reactant. For this experiment, an ozone-free 300 W Xe lamp (PLS-SXE 300C, Beijing Perfect light Co. Ltd.) with 420 nm cut-off filter was used as the light source (420 nm < λ < 760 nm) to trigger the photocatalytic reaction. During the illumination reaction process, about 3 mL reaction solution was collected at a certain time interval then centrifuged at 7000 rpm for 5 min to remove the catalyst completely. The reduction amount of Cr(VI) was analyzed on a Varian ultraviolet-visible-light (UV-vis) spectrophotometer (Cary-50, Varian Co.) and determined colorimetrically at 540 nm using the diphenyl-carbazide method [23]. The reduction ratio of Cr(VI) is calculated using the following expression:

$$\text{Reduction ratio of Cr(VI)} = (C_0 - C_t) / C_0 \times 100\%$$

Where C_0 and C_t are the absorbance intensities of illuminated for 0 and t min, respectively.

3. Results and discussion

3.1. Characterizations

XRD patterns of as-prepared samples and calculated MIL-68(Fe) are shown in Fig. 1. It is obvious that the diffraction peaks of MIL-68(Fe) match well with the calculated ones, indicating that the obtained samples are pure phase. In addition, the Fourier transformed infrared spectroscopy (FTIR) has been performed to analyze the molecular structure of MIL-68(Fe). As displayed in Fig. 2, the peak at 550 cm^{-1} can be ascribed to the stretching vibration of Fe–O, indicating the formation of a metal-oxo bond between the carboxylic group of terephthalic acid and the Fe(III) [24]. The peak at 748 cm^{-1} corresponds to C–H bonding vibrations of the benzene rings [25,26]. Moreover, the adsorption band of the carboxyl groups of the ligand coordinated to the metal centers (C=O, C–O) are

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