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A novel 3D flower-like Fe-photocatalyst with high degradative ability for water contaminant under visible light

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Abstract

A novel photocatalyst 2-amino-5-fluorobenzotrifluoride@Fe-based metal–organic framework (2A5F@Fe–MOF) was designed and synthesized, which exhibits excellent photocatalytic performance to degrade water contaminant rhodamine B (RhB) under visible light with 99.2% degradation rate after 2h. The photocatalyst was characterized by scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) as well as the analysis of morphological structure and chemical composition. Compared with pure Fe-MOF, the designed 2A5F@Fe-MOF photocatalyst appearance shows a transform from 2D to 3D, which maybe lead to the high photocatalytic activity toward RhB under visible light. The optimum conditions, such as ligand ratio, pH and concentration of RhB solution, were screened, also its degradation kinetic equations were built to give a typical reference for a large scale wastewater treatment.

Keywords
Photocatalyst; ligand; Fe-based MOF; rhodamine B; degradation
Introduction

Nowadays, dye wastewater pollution in textile industry has become a serious environmental problem, attracting more and more attention [1-3]. Rhodamine B (RhB) as a commercially used dye which has a certain representativeness in dye wastewater. According to the international agency for research on cancer (IARC), both inhalation and skin contact with RhB can cause acute and chronic toxic injuries [4].

In recent years, metal-organic frameworks (MOFs) have attracted extensive attention in sensor, catalysis, gas storage and photochemical devices due to its high specific surface area and adjustable porous size. Also, due to the different potential electric charge transfer transitions between ligands and metals, MOFs as a photocatalyst has attracted continuous attention [5-7]. A large number of research results reflect the growing interest in the application of MOF based composites and their derivatives in dye degradation [8-11]. Many methods for obtaining MOFs-related nanomaterials with high catalytic activity were studied. These approaches include the direct usage of MOFs exhibiting intrinsic photocatalytic activity (Ti-MOF, Fe-MOF, or Cu-MOF) [12-15] and the introduction of other components into MOFs to enhance dye adsorption or photocatalytic activity [16-18].

Due to iron's low toxicity and high biocompatibility, iron-based MOFs are particularly desirable for environmental applications [19-23]. Furthermore, iron oxides are rich in sources, cheap and have been widely used in magnetic fluid, magnetic recording, multifunctional catalysts and biomedicine. It is easily activated and absorbed by visible light for its narrow bandgap, therefore it can also be used as a visible light photocatalyst matrix. Zhang [24] used an ultrasonic assisted self-assembly preparation method to synthesize α-Fe$_2$O$_3$@g-C$_3$N$_4$ photocatalyst. The α-Fe$_2$O$_3$@g-C$_3$N$_4$ photocatalyst had a stronger optical absorption in the visible light region than pure graphitic carbon nitride (g-C$_3$N$_4$). He [25] synthesized the iron-based NH$_2$-MIL-88B (Fe) metal organic framework by a facile and rapid microwave heating
method. The photodegradation results show that NH$_2$-MIL-88B(Fe) can be used as a peroxidase-like catalyst for Fenton-like degradation of methylene blue (MB) in water. As we all known, visible light is the best source in nature to degrade contaminants, it is an interesting challenge to design the specific catalyst to absorb visible light. While, with the larger bandgap, the catalyst become more difficult to be excited by visible light. Therefore, designing novel ligands supported on such oxides to decrease the bandgap of catalyst, which can increase the possibility of photocatalyst excited by visible light, is a challenging task.

For our continuous interest and previous experience about developing novel photocatalyst to degrade water contaminants [26], we try to employ a simple ligand containing strong electron-withdrawing group which could be doped on Fe-MOF to decrease the band gap of photocatalyst so as to utilize solar energy directly. The commercial intermediate 2-amino-5-fluorobenzotrifluoride was selected to perform and verify this hypothesis. Fortunately, it works well when treating the pollutant RhB under visible light. It is worth mentioning that the interface of this novel ligand-doped photocatalyst has obvious appearance changes from 2D to 3D compared to the pure Fe-MOF, which maybe lead to the high photocatalytic activity toward RhB under visible light.

**Experimental**

2A5F@Fe-MOF was prepared according to the synthetic process below. Sodium dodecyl sulfate (5mmol, 1.45g) was added into the mixed iron (III) trichloride (40mmol, 6.48g) and the iron (II) dichloride tetrahydrate (20mmol, 3.98g) in deionized water (50mL) with stirring. After stirred for 1h, the solution of 2-amino-5-fluorobenzotrifluoride (10mmol, 1.79g) [n(Ligand): n(MOF)=1:2] in 50% (v/v) ethanol aqueous solution (20mL) was added. The solution was stirred overnight. The obtained brown precipitate was centrifuged, washed with deionized water, and dried at 80°C for 6h, successively. As a result, 50%2A5F@Fe-MOF was obtained. Fe-MOF, 25%2A5F@Fe-MOF and 100%2A5F@Fe-MOF were synthesized in the
same manner, only with the different amount addition of 2-amino-5-fluorobenzotrifluoride as the organic ligand.

The chemical composition of 2A5F@Fe-MOF composite was characterized by Fourier transform infrared (FT-IR, Bruker 55FT-IR). The scanning electron microscopy (SEM) measurements (S-4800, HITACHI) with an accelerating voltage of 15 kV was utilized to analyse morphologies structure. X-ray diffraction (XRD) patterns were recorded by X-ray diffraction (XRD, Bruker D8 Advance) patterns were recorded using Cu Kα radiation (40 kV and 40 mA) and scanning rate of 2°·min⁻¹. Chemical state of iron was analysed X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI). UV–Vis diffuses reflectance spectra was also obtained (DRS, Hitachi U-3900H).

The photocatalytic activities of photocatalysts were evaluated by the photo-degradation of rhodamine B (RhB) under visible light. In the typical experiment process, 0.1mg of the photocatalyst was added into the 20mL rhodamine B solution (20mg/L). Prior to irradiation, the suspensions were magnetically stirred for 30 minutes in the dark at room temperature to reach the adsorption-desorption equilibrium. The solutions were then irradiated with the solar simulator (Newport 94023A, USA). At specific time intervals of 20 minutes, 1mL of the solution was withdrawn from the system and centrifuged (4000rpm, 5min) to remove the photocatalyst particles. The degradation rate was monitored by UV-Vis spectrometer (Beckman Coulter DU730) at room temperature. The degradation efficiency (DE) was calculated using the equation: DE=[(A₀-Aₜ)/A₀] ×100%. Where A₀ is the initial absorbance of solution and Aₜ is the absorbance of solution at a specific time.

**Results and Discussion**

The morphology and microstructure of the photocatalyst were studied using SEM. As shown in Figure 1a, it can be easily observed that the pure Fe-MOF had a smooth layer macrostructure. And its microstructure still remained a 2D layer (Figure 1b). After the ligand
doping, this photocatalyst appearance turned to a 3D structure (Figure 1c), whose microscopic spectrum showed a flower-like structure (Figure 1d). This flower-like structure greatly increases the specific surface area of the photocatalyst, which is the photocatalytic reaction site, thereby enhancing the photocatalytic properties of Fe-MOF.

As shown in Figure 2, five peaks are observed in the XRD pattern of Fe-MOF. 26.9°, 35.42°, 43.3°, 56.1° and 61.3° (2Theta) are belong to the (220), (311), (400), (511) and (440) plane diffractions of Fe₃O₄ (JCPDS card No.19-0629), respectively. The XRD pattern of the 50%A5F@Fe-MOF shows the peak strength was decreased and part of the peak were disappeared compare with Fe-MOF. These findings imply that the main structure of Fe-MOF remains but a small part of the surface is covered by the ligand after doping, which may lead to a large increase in photocatalytic activity.

**Figure 1:** SEM images of Fe-MOF (a, b) and 50%A5F@Fe-MOF (c, d)
XPS spectra of Fe 2p was carried out to determine the Fe state in Fe-MOF. The results were shown in Figure 3 where ‘sat.’ represents the satellite peak in the XPS spectrum. All the elements were corrected by C 1s at 284.8 eV. The percentage of Fe$^{3+}$ and Fe$^{2+}$ were calculated to be 41.9% and 58.1%, respectively, using curve-fitting [27]. The decrease of Fe$^{3+}$ is mainly attributed to the washing process.

Uv-vis absorption spectra were shown in Figure 4. As we can see in Figure 4a, after the ligand 2A5F was doped, the visible light absorption capacity of Fe-MOF was greatly enhanced at
visible region. The direct bandgap energies ($E_g$) of Fe-MOF and 50\%2A5F@Fe-MOF were estimated to be 2.08 and 1.91eV respectively, using formula [28,29]:

$$\alpha h\nu = A(h\nu – E_g)^{1/2}$$

The decline of $E_g$ after ligand doping can effectively enhance the visible light excitation ability of photocatalyst, which was confirmed by following degradation experiment that degradation rate jumped from almost zero to 99.2%.

![Figure 4: (a) The UV–Vis diffuses reflectance spectra of Fe-MOF and 50\%2A5F@Fe-MOF, (b) the band gap energies](image)

FT-IR spectroscopy was carried out to confirm the existence of ligand on the as-prepared catalyst. The results indicate that the ligand is successfully loaded on the photocatalyst particles. The strong band at 1380 cm$^{-1}$, assigned to C-F stretching. And the bands at 1600 and 1480 cm$^{-1}$, assigned to skeleton vibration of benzene. The peak at 3450 cm$^{-1}$ is assigned to N-H bond. The absence of other two peaks near 2950 and 2850 cm$^{-1}$ corresponds to C-H stretching vibrations of benzene.

**Optimization of Photocatalytic conditions**
Ligand ratio of photocatalyst

Figure 5a shows the photocatalytic performance of 2A5F@Fe-MOF composites towards 20mg/L RhB solution under visible light irradiation, respectively. It is observed that the photocatalytic efficiency of as-prepared Fe-MOF is nearly close to zero. Moreover, with the presence of 2A5F@Fe-MOF, the degradation efficiency is increased. 50%2A5F@Fe-MOF has the highest degradation rate which reached a maximum value of 99.2% after 2h treatment. As shown in figure 5b, the first-order kinetics rate constant was calculated using the following equation [30]:

\[ k = -\ln\left(\frac{A_0}{A_t}\right) \]

where “k” is the degradation rate constant (min\(^{-1}\)). The degradation rate constants were 1.298*10^{-4} min\(^{-1}\), 1.038*10^{-2} min\(^{-1}\), 1.625*10^{-2} min\(^{-1}\) and 1.143*10^{-2} min\(^{-1}\) for Fe-MOF, 25%2A5F@Fe-MOF, 50%2A5F@Fe-MOF and 100%2A5F@Fe-MOF, respectively. 50%2A5F@Fe-MOF showed the highest degradation rate constant, which is 125 times higher than Fe-MOF (figure 5c). The recycle experiment also showed that 50%2A5F@Fe-MOF has excellent stability, the degradation efficiency of 20mg/L rhodamine solution remains at 92% after 5 runs (figure 5d).
The effect of pH on photocatalytic activity was determined by degrading 20mg/L RhB solution at seven pH values: 1.0, 3.0, 5.0, 7.0, 9.0, 11.0 and 13.0 (Figure 6). The degradation rate of RhB was 99.2% after 2 h treatment without pH adjustment (pH=7.0). The degradation rates were 0.8%, 1%, 3.1%, 80.1%, 54.5% and 37% when the initial pH values were 13.0, 11.0, 9.0, 5.0, 3.0 and 1.0 after 2h treatment, respectively. The degradation rate was lower under acidic solution and alkaline solution, while the degradation rate of neutral solution was the highest.

**Figure 5:** (a) effect of ligand ratio, (b) kinetic curves of the photocatalysts, (c) rate constant of the photocatalysts, (d) recycling studies of 50%2A5F@Fe-MOF

**Figure 6:** Photocatalytic degradation of RhB at different pH
Concentration of RhB solution

Figure 7 shows the catalyst has a high degradation rate for RhB with a concentration of less than 40 mg/L. The degradation rate decreased a lot when the concentration comes to 80 mg/L. This may due to the concentrations of photocatalyst were limited, which was not enough for the degradation with higher concentration.

![Figure 7: Photocatalytic degradation of RhB at different concentrations](image)

Proposed degradation mechanism

Figure 8 shows the proposed mechanism for the photogenerated charges transfer process in the 2A5F@Fe-MOF photocatalyst. When the photocatalyst is irradiated, photogenerated electrons excited from the Fe-MOF are transferred along the hydrogen bonds to the surface ligand molecules, where the oxygen(O₂) can be turned to superoxide radical(·O₂⁻), which reducing the probability of recombination with photogenerated holes. Resulting the photogenerated holes and superoxide radicals can further degrade rhodamine in the solution.
Conclusion

In this work, a novel photocatalyst 2A5F@Fe-MOF were developed for the water contaminant degradation. The morphological structure and photocatalytic performance of Fe–MOF shows significant changes after the ligand doping. The morphology of photocatalyst transformed from 2D layer to 3D flower-like. And the optimum conditions for RhB degradation were carried out for the large-scale degradation reference. The degradation rate reached 99.2% after 2h treatment when ligand ratio was 50%, pH was 7.0 and concentration of RhB was 20 mg/L. which means the ligand 2A5F remarkably improved the photocatalyst performance of Fe-MOF. Its impressive photocatalytic activity for the degradation of RhB proved that our initial assumption of designing ligand doped on Fe-MOF is feasible.

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