



Ultrathin graphene oxide encapsulated in uniform MIL-88A(Fe) for enhanced visible light-driven photodegradation of RhB



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A B S T R A C T

It is very important to design excellent heterojunction structure for the improvement of the photocatalytic performance. In this study, we report a facile approach of polymerizing the ultrathin graphene oxide on the surface of the MIL-88A(Fe) to form MIL-88A(Fe)/graphene oxide composite for enhancing the photocatalytic efficiency of organic molecules degradation. The optical graphene oxide doping content in MIL-88A(Fe)/graphene oxide hybrid is determined to be 9.0 wt%, which increases the surface area of the MOFs from 15.9 m²g⁻¹ to 408.9 m²g⁻¹ due to the emerging micropores, and the corresponding photocatalytic rate for RhB is 8.4 times higher than that of pure MIL-88A(Fe). Meanwhile, DMF-free MOF-based heterostructure could avoid secondary contamination in the photocatalytic application process, and the degree of RhB removal is maintained at about 100% after the five cycles of the reaction. Integrating the related electrochemical analysis and the active species trapping experiments, the decisive factors for the improved photocatalytic efficiency of MIL-88A(Fe)/graphene oxide may be the unique structural advantages of ultrathin graphene oxide sheets, compact and uniform interface contact, more adsorption sites and more reaction sites. This work provides a novel sight for preparing high-efficient and environment-stable photocatalysts by designing the surface heterojunction structure.

Keywords: MIL-88A(Fe); graphene; Visible light; Rhodamine B; heterojunction structure

1. Introduction

Metal organic frameworks (MOFs), formed by polydentate organic linkers and metal ions or metal clusters, are a class of advanced crystalline composite porous materials [1–3]. Owing to their high surface area, well-distributed but adjustable pores and easily tailored chemical properties, MOFs have many outstanding performances and potential applications in drug delivery, gas storage, molecular sensing, separation and catalysis [4–9]. Recently, MOFs have been used for light harvesting because they possess chromophores that can interact with light and undergo photochemical process after photo-excitation [10]. For instance, a well-known MOF-5 reported by the group of Garcia has been demonstrated to be a distinguished photocatalyst for phenol removal under UV light irradiation [11]. A Cu-doped ZIF-67 has been applied as a photocatalyst for the decolorization of methyl orange under visible

light [12]. Some Zr-based NH₂-UiO-66 MOFs have also displayed visible-light-driven photocatalysts for the degradation of organic pollutants and the reduction of Cr(VI) [13,14].

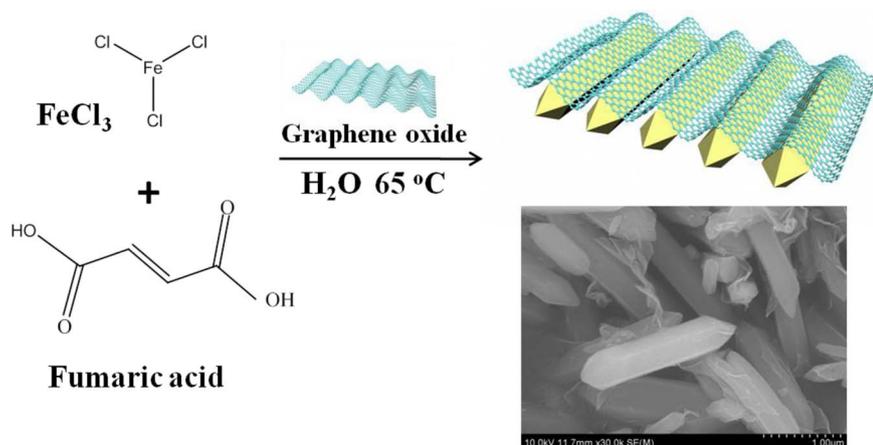
Of note, although some MOFs are capable of interacting with visible light in solar spectrum, the activities of those MOF photocatalysts are restricted by the relatively poor separation and migration of photo-generated electron-hole pairs. Up to now, many strategies have been used to improve the photocatalytic efficiencies of MOFs by inhibiting charge carriers recombination, such as surface modification and doping [15]. Among them, it is popular that the utilization of noble metal or metal oxide (such as Ag, Pt, Au, Pd) to improve the photocatalytic efficiency of MOFs by forming heterostructured photocatalysts [16,17], but the inevitable shortcomings of limited content and high price of noble metal constrain its practical application [17].

Alternatively, another feasible and significant strategy to enhance photogenerated charge carriers separation and thus enlarge their lifetime is the combination semiconductor with graphene oxide (GO) to form heterojunctions, owing to the superior charge carrier mobility,

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Scheme 1. XXX.

high specific surface area, and high electrical conductivity of GO [18,19]. It has reported that the photocatalytic applications of several GO-semiconductor (e.g., TiO_2 , ZnO , Bi_2WO_6 , CdS , WO_3 and MOFs) and those composites could enhance the photoreactivity. MIL-53(Fe)-graphene nanocomposites are prepared as efficient visible-light photocatalysts for the selective oxidation of alcohols [20]. A novel MIL-68(In)- NH_2 /graphene oxide composite is prepared as a visible-light-driven photocatalyst for the degradation of amoxicillin [21]. MIL-53(Fe)-reduced graphene oxide (M53-RGO) nanocomposites have been successfully fabricated by a facile and efficient electrostatic self-assembly strategy for improving the photocatalytic reduction of Cr(VI) [22]. Inspired by those good results, and for further investigate the synergistic effect between MOFs and GO, we have tried to explore other GO-based MOFs composites as highly efficient photocatalysts [23,24].

Up to date, there are several Fe-based MOFs have been successfully prepared, such as MIL-100 [25], MIL-101 [26], MIL-53 [27], MIL-88 B [28] and MIL-88A [29]. While most of the Fe-based MOFs are synthesized using N, N-dimethylformamide (DMF) as a solvent, if the solvent is not completely removed during the synthesis, DMF will cause secondary contamination in the application process. Thus, a DMF-free Fe-based MOF could be an appropriate MOF material for the design of MOFs/GO heterojunction structures. To the end, MIL-88A(Fe) is selected in this work because it can be prepared by the coordination of fumaric acid and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ just in the water. We introduced graphene oxide into the MIL-88A(Fe) to form MOFs/GO heterogeneous structures for enhancing the photocatalytic activity of the MOFs. The MIL-88A(Fe)/GO- H_2O_2 systems exhibit better photocatalytic efficiency for the removal of Rhodamine B (RhB) than that of pure MIL-88A(Fe)- H_2O_2 under visible light irradiation. The introduction of H_2O_2 as electron acceptor can significantly improve the photocatalytic RhB removal of MIL-88A(Fe). Meanwhile, GO played a significant part in the photocatalytic reaction as well. Moreover, the MIL-88A(Fe)/GO photocatalyst exhibits a high stability and reusability in aqueous solution.

2. Experimental

In this study, all the chemical reagents used were purchased from Sinopharm Chemical Reagent Co., Ltd., (China). And all chemicals and reagents in this research were of commercially available analytical grade and used without any further purification.

2.1. Preparation of photocatalysts

2.1.1. Synthesis of graphene oxide nanoribbons

Graphite oxide (GO) was prepared by the Hummers method with some modifications [30]. In a flask, 6.0 g Graphite was added into 140 mL of H_2SO_4 (98 wt%) and stirred in an ice bath for 10 min. 3.0 g sodium nitrate (NaNO_3) and 18.0 g potassium permanganate (KMnO_4)

were mixed into the flask and the reaction mixture was stirred at 20 °C for 3 h. Then the reaction temperature was raised to 35 °C. After 4 h, the reaction mixture was slowly diluted with 300 mL of water, and the reaction temperature rapidly rose to 95 °C. After another 2 hours, 40 mL of H_2O_2 (30 wt%) and 600 mL of water were dripped into the reaction system. The sample was collected by centrifugation. The precipitation was washed with 10% HCl, and then dialyzed for 7 days with water. After centrifugation, the particle was GO.

2.1.2. Preparation of MIL-88A(Fe)

MIL-88A(Fe) was prepared according to the literature with some modifications [31]. In a specific procedure, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.352 g) and $\text{C}_4\text{H}_4\text{O}_4$ (0.580 g) were mixed into 25 mL ultrapure water and then stirred by magnetic force till it turned into homogeneous solution, then it was put into autoclave and heated at 65 °C for 12 h. After cooling to room temperature, the sample was collected by centrifugation and dried under vacuum at 65 °C.

2.1.3. Synthesis of M88/GO nanocomposites

Scheme 1 shows a schematic diagram of the synthesis procedure. The MIL-88A(Fe)/Graphene oxide hybrids were prepared by a feasible hydrothermal reaction by controlling the mass ratios of MIL-88A(Fe) vs Graphene oxide. Firstly, a scheduled amount of GO powder was dissolved into 10 mL ultrapure water under ultrasonic conditions. Then $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.352 g) and $\text{C}_4\text{H}_4\text{O}_4$ (0.580 g) were added into 25 mL ultrapure water and stirred continuously, when it become homogeneous mixture, the GO solution was slowly dropped into the above solution and stirred vigorously for 2 h. Then it was put into hydrothermal conditions in an autoclave for 12 h at 65 °C. And the other procedure of the above solution remaining was the same as that of MIL-88A(Fe). The final products were labeled as M88/GO-1, M88/GO-5, M88/GO-9, and M88/GO-11 (the abbreviated numbers in the name represent the weight content of the GO for 1%, 5% , 9% , 11%).

2.2. Materials Characterization

The XRD patterns were performed using a XRD diffractometer (Bruker D8 ADVANCE) that was run at 40 mA and 40 kV using Cu K α radiation. The Fourier transform infrared (FT-IR) spectroscopy was conducted on Smart Omni-Transmission FTIR Spectrometric Analyzer. The morphology of the samples was obtained from a JEOL JEM-2010F transmission electron microscope (TEM) operating at 200 kV and a Hitachi FESEM-4800 scanning electronic microscopy (SEM). X-ray photoelectron spectroscopy (XPS) surveys were obtained by using a ESCALAB 250Xi system. UV–vis diffuse reflectance spectra (UV–vis DRS) were recorded by a UV-2600 UV–vis spectrometer and BaSO_4 was applied as a reflectance standard in the experiment. The photoluminescence (PL) spectra was conducted at an excitation wavelength

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