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Short Communication

In-situ ethylenediamine-assisted synthesis of a magnetic iron-based metal-organic framework MIL-53(Fe) for visible light photocatalysis

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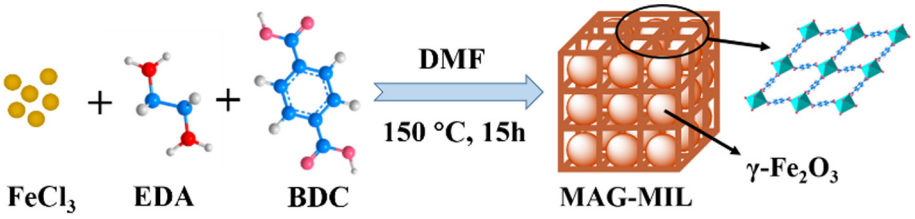
GRAPHICAL ABSTRACT

A superparamagnetic MIL-53(Fe) photocatalyst with a red-shift of the light absorption edge was synthesized by an in-situ ethylenediamine (EDA)-assisted solvothermal method.



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ABSTRACT

A novel magnetic MIL-53(Fe) photocatalyst (MAG-MIL) has been synthesized by an in-situ ethylenediamine (EDA)-assisted solvothermal method. The well dispersed γ-Fe_2O_3 nanoparticles embedded in the MAG-MIL framework contribute to a red shift of the light absorption edge as well as the superparamagnetism characteristic.

1. Introduction

Metal organic frameworks (MOFs), as a novel class of inorganic-organic hybrid materials, have aroused widespread interest due to their high surface areas, tunable porous sizes and open crystalline structures [1,2]. They are widely used in various application fields, such as adsorption, catalysis, sensing, energy storage, and drug delivery [3–7]. However, many MOFs materials can only be used in ultraviolet light photocatalysis because of their wide band gap [8–10]. Therefore, it is a great challenge to increase light harvesting ability of MOFs from ultraviolet light (UV) to visible light for further enhancement of photocatalytic activity. The modification of MOFs by ammoniating or hydroxylating the organic linkers has been reported to increase the photocatalytic activity, such as NH_2-MIL-125(Ti), NH_2-MIL-88B(Fe) and UiO-66-NH_2 (MIL and UiO stands for two kinds of MOFs materials) [11–13]. Furthermore, guest species, such as semiconductors, metal nanoparticles, organic photoactive materials, have been used to load on or into the matrices of MOFs to extend their spectral absorption [14–16].

MIL-53(Fe), as a visible-light sensitive MOF photocatalyst, has attracted increasing attention recently. However, the optical absorption band of MIL-53(Fe) is about 455 nm, which is limited

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for visible light photocatalysis [17–19]. Moreover, it is difficult to recycle MIL-53(Fe) due to its high dispersive nature. As we all know, magnetic materials are beneficial to recycling, improving their practical application [20–24]. It is therefore desirable to introduce magnetic γ-Fe_2O_3 nanoparticles to MIL-53(Fe) to extend its spectral absorption and superparamagnetic property for industrial applications. Ke et al. synthesized mercaptoacetic acid functionalized Fe_3O_4 magnetic nanospheres and then incorporated them into MIL-100(Fe) to gain Fe_3O_4@MIL-100(Fe) core-shell nanostructures [25,26]. Zhang et al. prepared Fe_3O_4 magnetic nanospheres and assembled the magnetic nanospheres onto the MIL-53(Fe) to obtain magnetic MIL-53(Fe) for electrocatalysis and photocatalysis [27]. Bezverkhyy et al. synthesized γ-Fe_2O_3/MIL-100(Fe) and γ-Fe_2O_3/MIL-53(Fe) composites using a novel hydrolysis and calcination approach [28]. These magnetic photocatalysts are green, cheap and more suitable for large scale industrial applications. However, those magnetic MIL-53(Fe) materials were synthesized by post-modification or multi-step reaction. Using one step in-situ method to prepare magnetic MOFs was not reported so far.

Herein, a facile in-situ solvothermal method was introduced to prepare magnetic MIL-53(Fe) (MAG-MIL) in this manuscript for the first time, in which ethylenediamine (EDA) was added as both ligand and surfactant. The crystal structure, morphology and the magnetic property of the prepared MAG-MILs were investigated. The photocatalytic activities of MAG-MILs were tested through degrading methylene blue (MB) under visible light irradiation. The results showed that the as-prepared MAG-MIL exhibited excellent photocatalytic activities. Moreover, the used MAG-MIL photocatalyst could be collected by magnet for reuse.

2. Experimental methods

2.1. Preparation of MAG-MILs

The preparation procedures of the catalysts are shown in Scheme 1. MIL-53(Fe) was synthesized by a solvothermal method according to the previous report [29]. In a typical experiment, a mixture of $FeCl_3$, terephthalic acid (BDC) and N,N-dimethylformamide (DMF) with a molar ratio of 1:1:280 was mixed and sonicated for a few minutes, then placed in a Teflon-lined steel autoclave, heating at 150 °C for 15 h. Light brown powder was obtained by centrifuging using DMF as solvent and then stirring in methanol for three days. Finally, the solid powder was heated at 150 °C overnight to remove guest molecules (H_2O, DMF, and methanol). As for MAG-MILs photocatalysts, the synthesis condition was the same as MIL-53(Fe) except for the addition of EDA and $FeCl_3$. The obtained catalysts with deep coffee color were noted as x-MAG-MIL (x presents the volume of added EDA).

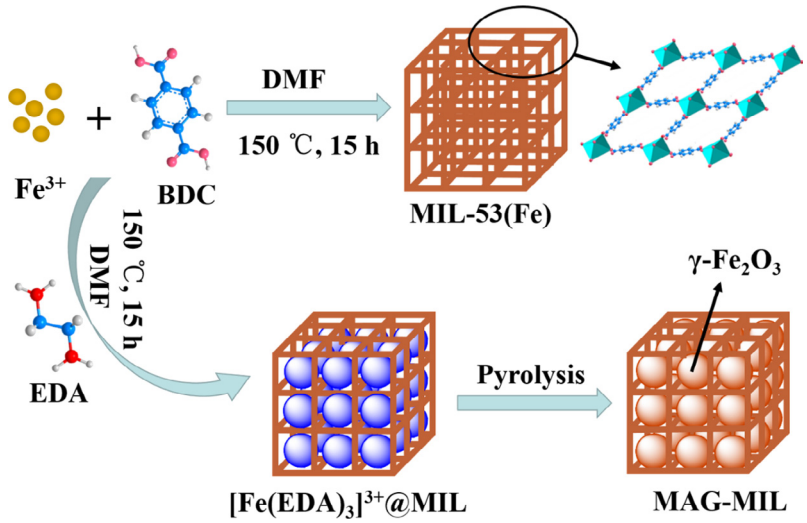
In this process, as both ligand and surfactant, EDA could reacted with Fe^{3+}, forming a relatively stable $[Fe(EDA)_3]^{3+}$ compound validated by previous report [30,31]. Then, BDC reacted with the excessive Fe^{3+}, forming MIL-53(Fe) outside of the $[Fe(EDA)_3]^{3+}$, namely $[Fe(EDA)_3]^{3+}$@MIL. This central compound $[Fe(EDA)_3]^{3+}$ could gradually be pyrolysised at higher temperature and vapor pressure, and finally transformed into γ-Fe_2O_3. Similarly, Wu et al. synthesized γ-Fe_2O_3@ZIF-8 via in situ pyrolysis of $Fe(acac)_3$@MOFs [32]. In their experiments, the ferric triacetylacetonate Fe $(acac)_3$ was directly added into the MOFs precursor sources and then pyrolysised under a flow of N_2 at 300 °C.

2.1. Photocatalytic experiments

To compare the photocatalytic activity of different photocatalysts, a series of photodegradation experiments were carried out under irradiation using a 500 W Xenon lamp with an UV cutoff fitter (λ < 420 nm) or a near-infrared light (NIR) cutoff filter (λ > 700 nm). In a typical photocatalytic experiment, 0.02 g catalyst was dispersed in 50 mL MB (10 mg L^{-1}) solution in a quart tube. Prior to the irradiation, the mixture was stirred for 40 min in the dark to reach adsorption equilibrium. Samples were collected at selected time intervals and the catalyst particles were removed by a magnetic field before analysis. The concentration of MB was analyzed with an UV–vis spectrophotometer at the maximum absorption wavelength of 664 nm.

3. Results and discussion

Typical powder X-ray diffraction (XRD) patterns of MIL-53(Fe) and MAG-MIL are shown in Fig. 1a. The diffraction peaks of MIL-53(Fe) were consistent with the previous literature [29]. For MAG-MIL, the diffraction peaks of MIL-53(Fe) exhibited a red shift. In addition, the diffraction peaks of the iron oxide were not obvious, owing to the fact that the magnetic nanoparticles were small and dispersed homogeneously in the framework of MIL-53(Fe). Fig. 1b illustrates the Fourier transform infrared (FT-IR) spectra of MIL-53(Fe) and MAG-MIL. The spectra of the materials exhibited bands (Ar C-H) assigning to aromatic groups at 3050 cm^{-1} and 748 cm^{-1} [27,29], and C=O stretching vibration at 1695 cm^{-1}



Scheme 1. Preparation of magnetic MIL-53(Fe) (MAG-MIL).