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UiO-66(Zr) coupled with Bi_2MoO_6 as photocatalyst for visible-light promoted dye degradation

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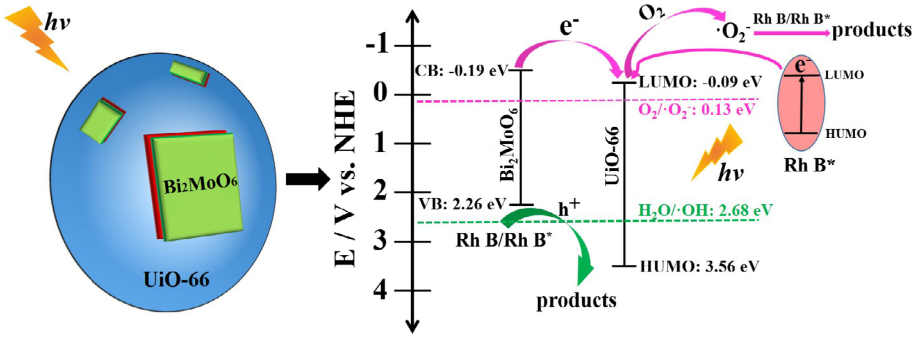
GRAPHICAL ABSTRACT

A novel Bi_2MoO_6/UiO-66(Zr) composite was prepared via electrostatic interaction induced self-assembly process. The Bi_2MoO_6/UiO-66(Zr) composite shows prior photocatalytic performance than parent materials, which could be ascribed to the efficient separation of photogenerated charge carriers resulted from the interaction between Bi_2MoO_6 and UiO-66(Zr).



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ABSTRACT

This study provides the first attempt to combine UiO-66(Zr) with Bi_2MoO_6 for the preparation of composite via electrostatic interaction induced self-assembly process. Synthesized products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscope (FT-IR), X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET) surface area analyse and UV–vis diffuse reflectance spectroscopy (UV–vis DRS). The photocatalytic activities of as-obtained Bi_2MoO_6/UiO-66(Zr) composites were assessed by degradation of Rhodamine B (Rh B) under the visible-light irradiation. Comparing to the pristine materials, the developed Bi_2MoO_6/UiO-66(Zr) composite with Bi:Zr molar ratio 2:1, labelled as BMUO-2, showed the best photocatalytic activity. It was supposed that the participation of Bi_2MoO_6 increased the use of solar energy and the existence of UiO-66(Zr) restrained the recombination rate of photo-generated electron-hole pairs. Moreover, Bi_2MoO_6/UiO-66(Zr) composite showed excellent stability and recyclability during cycling experiment. The mechanism and plausible pathway of Rh B degradation were also discussed in this paper.

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1. Introduction

Photodegradation based on semiconductor is believed to be one of the most promising strategies used for the elimination of water contamination since it is able to effectively degrade organic pollutants, what results in the production of CO_2 and H_2O as the final product [1,2]. A lot of conventional semiconductors, including TiO_2 [3], ZnO [4] and Cu_2O [5], have been applied in photocatalysis. However, they are often restrained by their low quantum yield under visible-light irradiation and poor absorptive properties for organic pollutants [6–8]. Metal-organic frameworks (MOFs), which are a new sort of hybrid porous materials, have generated rapid development since past two decades, because of their desired features, including very specific surface areas, designable framework architecture, tunable pore size and their possibility to be functionalized [9]. Particularly, the semiconductor behaviour of MOFs has attracted increasing research interests. Many MOFs, such as MOF-5 [10], MIL-53(Fe) [11], MIL-88(Fe) [12] and MIL-101(Fe) [13] could be excited under UV–visible light, due to their linker to metal cluster charge transfer (LMCT) [14]. However, the performance of MOFs is no equal as in the case of inorganic semiconductors because MOFs' are not efficient enough in the photo-generated charge separation and conversion of solar energy.

Heterostructures integration of MOFs with light-harvesting semiconductor materials has been recognized as an efficient way for the production of effective photocatalyst. Comparing with MOFs themselves, the hybrids display significant benefits, because of their synergistic effect. For example, the MIL-125(Ti) was formed a micro core-shell structure with In_3S_2, and the obtained composite was adopted as a photocatalyst for tetracycline's removal from water [15]. MIL-88(Fe) and MIL-53(Fe) were decorated by GO for the Rhodamine B (Rh B) decolorization under visible-light irradiation [16,17]. Ag/AgCl was embedded on MIL-101 for the Rh B degradation driven by visible light [18]. In these examples, MOF supported semiconductor composites display better photocatalytic performance comparing to the unsupported semiconductor materials. Therefore, MOFs is believed to be an ideal platform to support diverse semiconductor materials for the photocatalytic applications in water treatment.

UiO-66(Zr) is a zirconium-based MOF. UiO-66(Zr) not only possesses the excellent properties as the same as other MOFs, but also exhibits better thermal stability and chemical stability [19]. Additionally, UiO-66(Zr) shows high structural stability in water, what makes it a promising candidate for the photocatalysis process [20].

Recently, bismuth-based semiconductor has received extensive attention due to its great availability, non-toxicity and chemical inertness [21]. As a narrow band gap semiconductor (~2.6 eV), Bi_2MoO_6 is a promising candidate for harvesting the solar energy [22]. It has been used for decomposing organic pollutants [23], photo reduction of CO_2 [24] and water splitting [25]. However, the photocatalytic performance of Bi_2MoO_6 displays low quantum yield and thus it is not adequate enough for practical applications [26]. Its photocatalytic performance can be significantly improved via the construction of heterojunctions.

In this study, UiO-66(Zr) was used as a substrate for Bi_2MoO_6 synthesis. The Bi_2MoO_6/UiO-66(Zr) (BMUO) composites were obtained by using a hydrothermal method. Both the structure and optical properties of Bi_2MoO_6/UiO-66(Zr) composites were characterized, and their photocatalytic activity was tested by decomposing Rh B under the irradiation in visible-light. The results show that as-prepared Bi_2MoO_6/UiO-66(Zr) composite, defined as BMUO-2, has the greatest photodegradation efficiency. The enhanced photodegradation efficiency can be linked with the suppressed recombination rate of hole-electron pairs derived from the interface between Bi_2MoO_6 and UiO-66(Zr). Moreover, BMUO-2 showed excellent stability and recyclability in the cycling experiments. The plausible mechanism of photocatalysis was also investigated.

2. Experimental

2.1. Synthesis of UiO-66(Zr)

0.655 g of Terephthalic acid (BDC) and 1.025 g $ZrCl_4$ were dispensed in 50 mL N,N′-dimethylformamide (DMF). Obtained suspension was then transferred into a 100 mL Teflon-lined bomb and tempered for 24 h at 120 °C. The white product was cooled down to the room temperature, then was centrifuged and washed with DMF and Methanol repeatedly. Finally, the UiO-66(Zr) particles were dried under the vacuum for 12 h at 100 °C.

2.2. Preparation of Bi_2MoO_6/UiO-66(Zr) composites

Bi_2MoO_6/UiO-66(Zr) composites with different Bi:Zr molar ratio were prepared by a simple hydrothermal method. Typically, for obtaining Bi_2MoO_6/UiO-66(Zr) composites with Bi:Zr molar ratio of 1:1 (denoted as BMUO-1), 100 mg (0.0154 mmol UiO-66(Zr) (formula reported as $Zr_{24}O_{120}C_{192}H_{96}$) was dispersed in 25 mL of distilled water with the aid of ultrasonic. Then, 0.0460 g of Na_2MoO_4 were introduced and the whole mixture was stirred for 1 h. After that, 0.1793 g of $Bi(NO_3)_3{\cdot}5H_2O$ were added to the suspension and stirred for another 30 min. After that, the mixture was transferred to a 50 mL autoclave, which was heated for 5 h at 180 °C. At the end, the desired product was obtained by the filtration, and then washed with deionized water several times. Other composites with Bi:Zr molar ratios of 0.5:1 (denoted as BMUO-0.5), 2:1 (denoted as BMUO-2), and 3:1 (denoted as BMUO-3) were also prepared through a similar approach by adjusting the amount of the precursors for Bi_2MoO_6. Pristine Bi_2MoO_6 was also obtained by using the same procedure without the addition of UiO-66(Zr).

2.3. Characterization

The models of X-ray diffraction (XRD) concerning these samples were registered with Bruker D8 advance over the range 5–75° (2θ), with Cu Kα line (λ = 1.5406 Å) utilized as the source of radiation. The size and morphology of the catalyst were observed by scanning electron microscope (SEM) (ZEISS Merlin, Germany), using a Car Zeiss EVO LS 10 microscope. The composites and functional groups of Bi_2MoO_6/UiO-66(Zr) were measured by Fourier Transform Infrared Spectroscope (FTIR) using Vector 33 Bruker. The spectrum was recorded in transmission mode ranging from 4000 to 400 cm^{-1}. X-ray photoelectron spectroscopy (XPS) were performed with a PHI 1600 spectroscope using Mg Kα X-ray source for excitation. The Brunuare-Emmett-Teller (BET) scope of surface area was collected with a MicroActive ASAP 2460 at liquid nitrogen temperature. The total volume of pores were received at $P/P_0 = 0.99$. The diffused spectra of reflectance (UV–vis DRS) were measured with UV-4100 spectrometer ranging from 200 to 800 nm, with $BaSO_4$ as the reflectance standard material.

2.4. Evaluation of the photocatalytic activity

Photocatalytic performance of the as-prepared catalysts was investigated through the photocatalytic decomposition of Rh B aqueous solution. During the standard experiment, 15 mg of photocatalyst were dispersed in 30 ml of Rh B solution (10 mg/L). Prior the illumination, the mixture was stirred in darkness for 1 h in order to accomplish the equilibrium of adsorption-desorption. After that, the mixture was irradiated under visible light. A