



Metal-free efficient photocatalyst for stable visible-light photocatalytic degradation of refractory pollutant

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ABSTRACT

The photocatalytic performance of the star photocatalyst g-C₃N₄ is restricted by the insufficient solar light absorption, low surface area and the fast recombination of photogenerated electron-hole pairs. The present study developed a facile in situ method to construct hexagonal boron nitride (h-BN) decorated g-C₃N₄ metal-free heterojunction with the aim to greatly enhance the surface area and promote the charge separation. The physical, chemical and optical properties of the resulted samples were thoroughly characterized. The photocatalytic performance of h-BN/g-C₃N₄ composites were evaluated under visible light irradiation using antibiotic tetracycline (TC) and rhodamine B (RhB) as target pollutants. Results showed that h-BN/g-C₃N₄ composites exhibited much higher photocatalytic activity than pure g-C₃N₄ and h-BN. The optimum photocatalytic efficiency of BC-3 sample for the degradation of TC was about 2.3 and 60.3 times higher than that of individual g-C₃N₄ and h-BN, respectively. Meanwhile, it was about 7.3 and 11.8 times higher than that of individual g-C₃N₄ and h-BN for RhB degradation, respectively. The enhanced photocatalytic activity of h-BN/g-C₃N₄ composite is mainly attributed to the larger surface area and the unique physicochemical properties of h-BN nanosheet which acts as a promoter for photoexcited holes transfer. This work indicates that the metal-free h-BN/g-C₃N₄ hybrid photocatalyst is a promising material in wastewater control.

1. Introduction

Due to the industrialization and population growth, a large amount of poisonous and hazardous pollutants are produced, which has become a serious environmental problem in many countries [1]. Nowadays, worldwide attention has been drawn to develop the state-of-the-art technologies to degrade toxic and hazardous chemicals in various wastewaters. The most popular Fenton process can generate hydroxyl radicals to completely decompose organic compounds into water and carbon dioxide [2]. However, the traditional Fenton reaction requires large amounts of chemical reagents and suffers from strict pH requirement (pH ~ 3) [3,4]. Recently, much attention has been focused on the photocatalytic strategy for environment purification, as solar energy is an inexhaustible and environmentally friendly energy resource [5–8]. At present, most photocatalysts are metal oxides, sulfides and nitrides with d0 or d10 transition metal cations which have the ability to generate hydroxyl ($\cdot\text{OH}$) and superoxide anion radicals ($\cdot\text{O}_2^-$) under light irradiations to degrade or convert pollutants (such as

heavy metals and organic compounds) into environmentally friendly compounds [9–11]. Unfortunately, most of these metal-based catalysts are active only under ultra-violet irradiation which only represents 5% intensity in solar energy, while others absorbing visible light are not stable during the reaction process: for example photocorrosion occurs in metal sulfides [12–14]. Photocatalysts for practical use with relatively high productivity have not yet been found. Searching and optimizing highly efficient photocatalysts is urgently needed.

Recently, metal-free graphitic carbon nitride (g-C₃N₄) with a visible-light driven band gap and proper band edges has emerged as a new class of photocatalyst [15]. In general, g-C₃N₄ is typically prepared by the polycondensation of nitrogen-rich organic precursors such as cyanamide, dicyandiamide, guanidine hydrochloride, melamine, urea and thiourea [15–19]. It can exhibit the ability of photocatalytic hydrogen/oxygen evolution from water splitting in the presence of sacrificial reagents and photodegradation of organic pollutants under sunlight irradiation [20,21]. However, it is worth noting that bulk g-C₃N₄ photocatalyst shows a low photocatalytic activity due to the insufficient

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solar light absorption, low surface area and the fast recombination of photogenerated electron-hole pairs. In order to increase the activity, many strategies such as introducing heteroatoms [6], coupling with other semiconductors [22], modified with carbon materials [23], controlling morphology [24] have been used, and g-C₃N₄-based heterojunction photocatalysts have shown encouraging activity improvement. It is proposed that the increased photocatalytic activity of the heterojunction may be attributed to the effective separation of the photoexcited carriers which are transferred into valence band (VB) and conduction band (CB) of opposite semiconductor respectively due to their potential difference of VB and CB [25,26]. Therefore, scientists have made significant efforts to improve the photocatalytic activity of g-C₃N₄ by coupling it with other semiconductors, such as TiO₂ [22], Bi₂O₂CO₃ [27], ZnIn₂S₄ [28], Bi₄Ti₃O₁₂ [29] and Ag₃PO₄ [30]. In recent years, some two-dimensional carbon materials, such as carbon nanotube, graphene and carbon dots, have been also used as an electron transfer channel for g-C₃N₄ to accelerate the separation of photoinduced charge carriers and obtain efficient metal-free photocatalysts [4,23,31–34]. Xu et al. prepared a novel multi-walled carbon nanotubes (CNT) modified white C₃N₄ composite with enhanced visible-light-response photoactivity for methylene blue degradation [31]. The degradation rate of the CNT/white C₃N₄ photocatalyst is almost 8.1 times as high as that of the white C₃N₄, which is caused by the efficient separation of the photo-generated charge carriers between C₃N₄ and CNT. Liao et al. fabricated metal-free graphene-carbon nitride hybrids by sonochemical approach for photodegradation of rhodamine B and 2, 4-dichlorophenol in water [33]. The photodegradation rates are much enhanced due to that the GO acts as a separation centre and electron acceptor in the GO/g-C₃N₄ hybrid. Fang et al. prepared carbon dots modified g-C₃N₄ hybrid by using carbon dots and dicyandiamide as precursor, in which carbon dots act as electron-sinks, preventing the recombination of photo-generated electron-hole pairs and thus enhancing the photocatalytic activity of g-C₃N₄ [23].

Hexagonal boron nitride (h-BN) is also a kind of two-dimensional metal-free material, which is similar to layered-structure graphene and has unique physicochemical properties, such as high stability, non-toxicity, low density and thermal conductivity [35,36]. In the recent researches, h-BN is reported to be a robust substrate for semiconductor photocatalysts [37–42]. More importantly, h-BN will be electronegative when the bulk h-BN is exfoliated into two-dimensional nanosheets. In this study, h-BN powder can be strongly attracted by glass due to the electrostatic interaction. This result confirms that h-BN is electronegative. Furthermore, the negatively charged h-BN nanosheets will attract the photoexcited holes and promote the separation efficiency of photoexcited electron-hole pairs [35,41]. It is different from the above conductive carbon materials (carbon nanotube and graphene) which have also been applied for accelerating the separation of photoinduced charge carriers by serving as an electron transfer channel recently [4,31–34]. Because these carbon materials exhibit high electron mobility and storing capacity, the photocatalytic activity of g-C₃N₄ can be significantly enhanced by coupling with these carbon materials. However, considering the characteristic recombination time of surface h⁺ (about 10 ns) is much shorter than that of e⁻ (about 100 ns) [43], increasing the transfer of h⁺ may be more crucial for the improvement of the photocatalytic activity, especially for the degradation reactions because the oxidation efficiency is usually determined by the number of interfacial holes. Theoretical and experimental work has confirmed that the negatively charged BN derives from stable defects associated with nitrogen vacancies (N edged triangle defects) or carbon impurities [35,37–42]. However, the attempt to construct h-BN nanosheet decorated graphitic carbon nitride as an efficient metal-free photocatalyst for the removal of pollutants has still never been reported.

Herein, we have firstly prepared metal-free h-BN nanosheet/g-C₃N₄ heterojunction photocatalysts by a facile in-situ growth strategy. The physical, chemical and optical properties of the resulted samples were thoroughly characterized with XRD, XPS, UV-vis DRS, BET, SEM, TEM,

PL, ESR and so on. The photocatalytic performance of h-BN/g-C₃N₄ composites were evaluated under visible light irradiation using TC and RhB as target pollutants. It could be found that h-BN/g-C₃N₄ composites showed much higher photocatalytic activity than pure g-C₃N₄ and h-BN. Furthermore, based on our experimental results, a probable photocatalytic mechanism was also proposed. The key role of h-BN for the improved photocatalytic performance was explored and the main active species were determined.

2. Experimental

2.1. Synthesis of the photocatalysts

All chemical reagents were analytical grade and used without further purification. h-BN powders used in this study were supplied by Chinese Macklin Chemical Reagent Co. The metal-free h-BN nanosheet/g-C₃N₄ heterojunction photocatalysts were prepared by a facile calcination strategy. Specifically, a certain amount (1.0 g) of dicyandiamide and different amount of h-BN were added into an agate mortar and grounded together. The resultant powders were transferred to a covered crucible, then calcined at 550 °C for 4 h with a heating rate of 10 °C/min [44]. After being cooled to room temperature, the resulting products were collected and milled into powder in an agate mortar for further use. To make clarity, the h-BN/g-C₃N₄ composites with expected h-BN contents of 1.0, 1.5, 2.0, 4.0, 12, and 20 mg were referred to as BC-1, BC-2, BC-3, BC-4, BC-5 and BC-6, respectively. XPS analysis was used to determine the content of h-BN in the h-BN/g-C₃N₄ composites. The results indicated that the mass contents of h-BN in BC-1 to BC-6 were 0.25%, 0.37%, 0.48%, 0.99%, 2.28%, and 4.53%, respectively. For comparison, h-BN nanosheet was obtained similarly but without dicyandiamide and bulk g-C₃N₄ powders were prepared similarly but without the addition of h-BN.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns were recorded using Bruker AXS D8 advance diffractometer operating with Cu-Kα source to investigate the crystal structure of the samples. The morphologies of resulting samples were characterized by a field emission scanning electron microscopy (SEM) (JSM-7001F, Japan) and transmission electron microscopy (TEM) (F20, USA). The X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific, UK) was carried out to analyze the surface electronic state. The specific surface area of these samples was characterized from the nitrogen absorption-desorption data and Brunauer-Emmett-Teller (BET) measurement (ASAP2020, Micromeritics, USA). UV-vis diffuse-reflectance spectra (UV-vis DRS) of as-synthesized samples were recorded in the range of 200–800 nm with a Varian Cary 300 spectrometer equipped with an integrating sphere. Photoluminescence (PL) spectroscopy was measured at the excitation wavelength of 350 nm on PerkinElmer LS-55 spectrofluorimeter at room temperature. Photocurrent measurements were performed on a CHI 660D electrochemical workstation (Shanghai Chenhua, China) using a three-electrode cell with the nanostructure materials on FTO as the working electrode, saturated Ag/AgCl and platinum electrode as the counter electrode and the reference electrode, respectively. The concentration of intermediate product H₂O₂ detected by the test paper (Merck, Germany). The electron spin resonance (ESR) signals were examined on a Bruker ER200-SRC spectrometer under visible light irradiation ($\lambda > 420$ nm).

2.3. Photocatalytic experiments

The photocatalytic measurements were carried out by using TC and RhB as target pollutants under visible light irradiation. A 300 W Xenon lamp (Beijing China Education Au-light, Co., Ltd.) with a 420 nm cutoff filter was used as the visible-light source. In a typical procedure,

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