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In-situ polymerization for PPy/g-C_3N_4 composites with enhanced visible light photocatalytic performance

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ABSTRACT

Polypyrrole-modified graphitic carbon nitride composites (PPy/g-C_3N_4) are fabricated using an *in-situ* polymerization method to improve the visible light photocatalytic activity of g-C_3N_4. The PPy/g-C_3N_4 is applied to the photocatalytic degradation of methylene blue (MB) under visible light irradiation. Various characterization techniques are employed to investigate the relationship between the structural properties and photoactivities of the as-prepared composites. Results show that the specific surface area of the PPy/g-C_3N_4 composites increases upon assembly of the amorphous PPy nanoparticles on the g-C_3N_4 surface. Owing to the strong conductivity, the PPy can be used as a transition channel for electrons to move onto the g-C_3N_4 surface, thus inhibiting the recombination of photogenerated carriers of g-C_3N_4 and improving the photocatalytic performance. The elevated light adsorption of PPy/g-C_3N_4 composites is attributed to the strong absorption coefficient of PPy. The composite containing 0.75 wt% PPy exhibits a photocatalytic efficiency that is 3 times higher than that of g-C_3N_4 in 2 h. Moreover, the degradation kinetics follow a pseudo-first-order model. A detailed photocatalytic mechanism is proposed with ·OH and $\cdot O_2^-$ radicals as the main reactive species. The present work provides new insights into the mechanistic understanding of PPy in PPy/g-C_3N_4 composites for environmental applications.

1. Introduction

Environment pollution and the energy crisis are two major challenges currently confronting human society. Recently, photocatalytic technologies have been shown to effectively decompose hazardous organic contaminants and address environmental and energy concerns to some extent [1]. Traditional semiconductor photocatalysts mostly comprise inorganic compounds, such as metal oxides, sulfides, nitrides, phosphides and their complexes. Most of them contain expensive metal elements [2]. Research into new types of inexpensive non-metal photocatalysts with high quantum efficiencies, high visible light usage, and high stability has garnered considerable interest worldwide in the field of photocatalysis [3].

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Among the various available photocatalysts, graphitic carbon nitride (g-C_3N_4) is a promising non-metal photocatalyst that has received significant attention owing to its suitable band gap energy (2.7 eV), high thermal stability, excellent electronic properties [4], as well as the unique 2D structure favorable for hybridization [5]. Therefore, g-C_3N_4 is multifunctional with broad applications in water splitting activity [6,7], energy conversion [8], and the degradation of environmental contaminants [9–11]. However, the photocatalytic efficiency of pure g-C_3N_4 is far from ideal owing to its low surface area and the fast recombination of photogenerated electron-hole pairs, which could be attributed to the classical thermal polymerization synthesis method [12]. Hence, it is necessary to develop strategies to improve the photocatalytic activity of g-C_3N_4 by balancing the relationship between electron transportation and light absorption. Therefore, extensive efforts have been devoted towards modifying g-C_3N_4 to enhance the photocatalytic activities, such as by doping with metal or non-metal elements [13–15], developing a heterojunction structure [16–19], introducing noble metals [20], and copolymerizing with other semiconductors [21]. Among them, copolymerization has been demonstrated to be efficient in modulating the electronic structure of g-C_3N_4 and the photocatalytic performance [22].

With regard to copolymerization, conducting polymers can serve as good candidates for the effective separation of photogenerated carriers from g-C_3N_4. Conducting polymers are important organic semiconductors with a unique delocalized π-π* conjugated electronic structure and excellent electrical, electrochemical, and optical properties; they have been applied in various electrocatalysts and photocatalysts, such as dye sensitized solar cells [23] and biosensors [24]. For example, He et al. [25] synthesized polyacrylonitrile (g-PAN)/g-C_3N_4 composites through the thermal condensation of PAN and melamine to enhance the visible light photocatalytic performance for H_2 evolution. Hu et al. [26] developed a simple sonochemical approach to prepare g-C_3N_4 and polythiophene (Ptp) nanocomposites, which manifested better photocatalytic activity and stability than pure g-C_3N_4, owing to the strong interaction between polythiophene and g-C_3N_4. Ge et al. [27] synthesized polyaniline (PANI)/g-C_3N_4 compounds by *in-situ* deposition polymerization, which led to an improved photogenerated carrier separation. Among the aforementioned polymers, polypyrrole (PPy) possesses good environmental stability, high conductivity, and interesting redox properties, and it is easy to fabricate under various conditions [28]. Such characteristics make it a promising material that could be applied in photocatalyst modification to enhance pollutant degradation. For example, Torki et al. [29] investigated the photocatalytic performance of a NiS and NiS-immobilized magnetite PPy core/shell (Fe_3O_4@PPy) in cephalexin degradation. Wang et al. [30] found that PPy-modified $Bi_2O_2CO_3$ showed enhanced photocatalytic performance compared with the pure $Bi_2O_2CO_3$. Pruna et al. [31] introduced a simple two-step electrochemical approach to fabricate ZnO/PPy-GO hybrid shell arrays with better photoactivity. In addition, some research on PPy/g-C_3N_4 composites with Ag nanoparticles has also been conducted [32,33]. The Ag nanoparticles anchored between g-C_3N_4 and PPy acted as electron transfer mediators that could facilitate the charge carrier separation. Nevertheless, some of the modification methods for PPy/g-C_3N_4 composites include complicated synthetic steps or introduce other semiconductors and noble metals, thus decreasing their practical utility. Therefore, systematic research on the modification of g-C_3N_4 with PPy is of great significance.

Herein, a series of novel PPy/g-C_3N_4 composites were prepared through a facile *in-situ* polymerization method; they exhibited improved photocatalytic activity in the degradation of methylene blue (MB) under visible light illumination compared with that of g-C_3N_4. The prepared composites were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET) specific surface area spectrometry, ultraviolet-visible diffuse reflection spectroscopy (UV-vis DRS), photoluminescence (PL) spectroscopy, and photocurrent response. The effect of sodium dodecyl benzenesulfonate dose of PPy in the fabrication of the composites was also evaluated. Moreover, the main reactive species in the degradation reaction were detected by electron spin resonance (ESR) spectroscopy, and a possible mechanism for the enhanced visible light photodegradation of MB by PPy/g-C_3N_4 composites was proposed. The present work provides new insights into the mechanistic understanding of PPy in PPy/g-C_3N_4 composites for environmental applications.

2. Experimental

2.1. Materials

Analytically pure chemicals, including melamine, ferric chloride hexahydrate, sodium dodecyl benzenesulfonate (SDBS), methylene blue (MB), and absolute ethanol, were all purchased from Chengdu Kelong Chemical Agents (China) and used as received without further purification. Pyrrole (chemically pure grade) was from Shanghai Aladdin Reagent Co., Ltd. and distilled twice to avoid coloration under lower pressures (vacuum). Deionized water was used in all of the experiments.

2.2. Catalyst preparation

A certain amount of melamine was dissolved in deionized water, and ultrasonically dispersed for 1 h. The dispersion was dried at 60 °C for 12 h, and then calcined in an alumina crucible at 520 °C for 5 h (10 °C min^{-1}) to give g-C_3N_4 as a powder. Subsequently, 4 g of the prepared g-C_3N_4 powder and 0.2 g SDBS were dissolved in 100 mL deionized water, and ultrasonically dispersed for 20 min. Then a specific amount of pyrrole was added to the mixture under constant stirring in 200 mL ice water (0 °C). After an appropriate contact time, 10 mL of a specific concentration of aqueous ferric chloride was added drop-wise into the aforementioned solution. After 2 h, a significant change in the color of the solution from light yellow to light gray was observed. The mixture was still precipitated for 1 h, then filtered under vacuum and washed several times with