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In-situ polymerization for PPy/g-C₃N₄ composites with enhanced visible light photocatalytic performance

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ABSTRACT

Polypyrrole-modified graphitic carbon nitride composites (PPy/g-C₃N₄) are fabricated using an *in-situ* polymerization method to improve the visible light photocatalytic activity of g-C₃N₄. The PPy/g-C₃N₄ 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-C₃N₄ composites increases upon assembly of the amorphous PPy nanoparticles on the g-C₃N₄ surface. Owing to the strong conductivity, the PPy can be used as a transition channel for electrons to move onto the g-C₃N₄ surface, thus inhibiting the recombination of photogenerated carriers of g-C₃N₄ and improving the photocatalytic performance. The elevated light adsorption of PPy/g-C₃N₄ 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-C₃N₄ in 2 h. Moreover, the degradation kinetics follow a pseudo-first-order model. A detailed photocatalytic mechanism is proposed with ·OH and ·O₂⁻ radicals as the main reactive species. The present work provides new insights into the mechanistic understanding of PPy in PPy/g-C₃N₄ composites for environmental applications.

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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]. Tradi-

tional 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-C₃N₄) 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-C₃N₄ 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-C₃N₄ 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-C₃N₄ by balancing the relationship between electron transportation and light absorption. Therefore, extensive efforts have been devoted towards modifying g-C₃N₄ 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-C₃N₄ 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-C₃N₄. 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-C₃N₄ composites through the thermal condensation of PAN and melamine to enhance the visible light photocatalytic performance for H₂ evolution. Hu et al. [26] developed a simple sonochemical approach to prepare g-C₃N₄ and polythiophene (Ptp) nanocomposites, which manifested better photocatalytic activity and stability than pure g-C₃N₄, owing to the strong interaction between polythiophene and g-C₃N₄. Ge et al. [27] synthesized polyaniline (PANI)/g-C₃N₄ 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 (Fe₃O₄@PPy) in cephalixin degradation. Wang et al. [30] found that PPy-modified Bi₂O₂CO₃ showed enhanced photocatalytic performance compared with the pure Bi₂O₂CO₃. 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-C₃N₄ composites with Ag nanoparticles has also been conducted [32,33]. The Ag nanoparticles anchored between g-C₃N₄ and

PPy acted as electron transfer mediators that could facilitate the charge carrier separation. Nevertheless, some of the modification methods for PPy/g-C₃N₄ 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-C₃N₄ with PPy is of great significance.

Herein, a series of novel PPy/g-C₃N₄ 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-C₃N₄. 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-C₃N₄ composites was proposed. The present work provides new insights into the mechanistic understanding of PPy in PPy/g-C₃N₄ 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-C₃N₄ as a powder. Subsequently, 4 g of the prepared g-C₃N₄ 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

20 mL absolute ethanol and 100 mL deionized water. Finally, the composites were dried in an oven for 12 h at 60 °C. The resulting composites were labeled as XPPy/g-C₃N₄, where *X* represents the mass ratios of pyrrole and g-C₃N₄ for 1, 0.75, 0.5, and 0.25 wt%. PPy/g-C₃N₄ composites with different amounts of added SDBS (*e.g.*, 0.1, 0.2, and 0.3 g) were also prepared using the same method.

2.3. Characterization

The crystal structures and phase composition were characterized by X-ray diffraction with Cu *K*_α radiation (XRD-6100, Shimadzu, Japan). The chemical bonds of the samples were analyzed by FT-IR (IR Prestige-21, Shimadzu, Japan). The morphology and microstructure of the prepared products were measured by SEM (JSM-7000F, JEOL, Japan) and TEM (JEM-2100F, JEOL, Japan). The specific surface area and pore diameter distribution of the as-prepared samples were calculated by N₂ adsorption-desorption analysis (BET-BJH, ASAP 2020, Micromeritics, USA) at −196 °C. The optical properties and band gaps were examined by UV-vis DRS (UV-2550, Shimadzu, Japan) using BaSO₄ as the reference [16]. The PL (Hitachi F-7000, Japan) spectra of the samples were measured at room temperature under an excitation wavelength of 350 nm. The photocurrent response analysis was carried out by an electrochemical workstation (CHI 660E, China) with a three-electrode cell system equipped with an LED light as the visible light source. The working electrode with an area of 1 cm², Pt wire and saturated calomel electrode were used as the counter and reference electrodes, respectively, and 0.1 mol L^{−1} Na₂SO₄ acted as the electrolyte. The ESR signals of the radicals spin-trapped with 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) were measured using an ESR JES-FA200 spectrometer (JEOL, Japan). A methanol dispersion was used for DMPO-•O₂[−] and an aqueous dispersion was used for DMPO-•OH.

2.4. Photocatalysis test

The photocatalytic degradation of MB was conducted using a 12-W LED lamp (light intensity was 28 mW cm^{−2} with a light distance of 15 cm). The desired catalyst (0.05 g) was added into 50 mL of the dye aqueous solution containing 10 mg L^{−1} MB. The mixture was magnetically stirred until a homogeneous suspension was obtained. MB molecules on the surface of the catalyst reached adsorption-desorption equilibrium after 1 h in a dark chamber where the concentration of the MB aqueous solution remained stable; the 2 h experiment under visible light was conducted immediately after equilibrium was reached. Meanwhile, 5 mL aliquots of the suspensions were collected at given time intervals for target dye concentration analysis immediately after centrifugation (5000 r min^{−1}, 5 min). The MB concentration was determined by UV/vis spectroscopy at its characteristic wavelength of 662 nm [27]. The degradation rate (*η*) of MB was calculated as follows:

$$\eta = (1 - C_t/C_0) \times 100\% \quad (1)$$

where *C*₀ is the concentration of the dye solution adsorption-desorption equilibrium, and *C_t* is the concentration of the

dye solution at time *t* after the photocatalytic reaction [30].

3. Results and discussion

3.1. Microstructure characterization of composites

3.1.1. XRD analysis

Fig. 1 shows the typical XRD patterns of the pure g-C₃N₄, 0.75PPy/g-C₃N₄, and PPy samples. Two distinct diffraction peaks of pure g-C₃N₄ appeared at 13.1° and 27.6° and were indexed as the (100) and (002) lattice planes, respectively [34]. The diffraction of the (002) lattice plane corresponded to the interlayer accumulation of stacked conjugated aromatic compounds, which commonly represents a graphitic structure. The (100) lattice plane corresponded to the *tri-s*-triazine unit structure, which was related to the experimental precursor of melamine [35]. The *tri-s*-triazine ring structure effectively reduced the carbon–nitrogen bond reaction barrier to promote the growth of the graphitic layer crystal structure [13]. The 0.75PPy/g-C₃N₄ sample exhibited similar peak positions to those of pristine g-C₃N₄, which demonstrated that modification with PPy did not change the lattice structure of g-C₃N₄, but affected the crystal growth and reduced the crystallinity, as noted by the decreasing diffraction intensity. In addition, no PPy diffraction peaks were observed, which should be ascribed to the small amount of the polymer with amorphous particles.

3.1.2. FT-IR analysis

To further verify the interaction between PPy and g-C₃N₄, FT-IR spectra were obtained, as shown in Fig. 2, to investigate the chemical bonding. The same characteristic peaks appeared in pure g-C₃N₄ and the 0.75PPy/g-C₃N₄ composite. The peak at 807 cm^{−1} was assigned to the out-of-plane stretching of the *tri-s*-triazine unit. The series of peaks located at 1627, 1406, 1315 and 1246 cm^{−1} corresponded to the typical C(*sp*²)–N, C(*sp*²)=N stretching modes of g-C₃N₄ [36]. The peaks of PPy, located at 1529 and 1301 cm^{−1}, were attributed to the symmetric and antisymmetric ring-stretching modes of the C=C and C–H vibrations in the pyrrole ring, respectively. The peak at

Fig. 1. XRD patterns of the pure g-C₃N₄, PPy, and 0.75PPy/g-C₃N₄ samples.

Fig. 2. FT-IR spectra of the pure g-C₃N₄, PPy and 0.75PPy/g-C₃N₄ samples.

1035 cm⁻¹ was attributed to the C-N heterocyclic stretching vibration and that at 916 cm⁻¹ corresponded to the double polarization state of PPy [24]. The vibration peaks of the 0.75PPy/g-C₃N₄ composite were slightly stronger than those of pure g-C₃N₄, which was proposed to be because PPy was loaded on the g-C₃N₄ surface and the peaks of PPy and g-C₃N₄ overlapped with each other owing to their similar molecular structures. In short, FT-IR analysis supported that g-C₃N₄ and PPy co-existed in the as-prepared samples.

3.1.3. Micromorphology analysis

The surface morphologies of the samples were examined by SEM and TEM analysis. As shown in Fig. 3(a) and (b), the as-prepared pure g-C₃N₄ exhibited a smooth bulk layer structure, which was similar to the analogue graphite [37] with an irregular shape [38]. The PPy particle size was much smaller than that of g-C₃N₄. As for pure PPy and the 0.75PPy/g-C₃N₄ composite, small amorphous PPy particles were observed on the thin sheet-like g-C₃N₄ surface, which confirmed the composite structure illustrated in Fig. 3(e) and (f). No obvious agglomeration was observed in Fig. 3(c) and (d). The junction between g-C₃N₄ and PPy can increase the contact area [13], which may facilitate the charge transfer and inhibition of electron-hole recombination.

3.1.4. Nitrogen adsorption-desorption analysis

The specific surface area and pore structure of the as-selected samples were determined using nitrogen adsorption-desorption isotherms, as shown in Fig. 4. The 0.75PPy/g-C₃N₄ and g-C₃N₄ samples exhibited type-IV isotherms with H3 hysteresis loops at high relative pressures (*i.e.*, between 0.5 and 1.0), which demonstrated the presence of mesopores (2–50 nm) and macropores (>50 nm) [Fig. 4] [26,39]. Meanwhile, the relative pore-size distribution curves, which are presented in the inset of Fig. 4, were determined to calculate the broader pore diameter distribution at 1–140 nm. The mesopores of pristine g-C₃N₄ and 0.75PPy/g-C₃N₄ were mainly observed with sizes of 3.48 and 3.50 nm, while the wider mesopores were observed with sizes between 20 and 40 nm.

Fig. 3. SEM and TEM images of the prepared pure g-C₃N₄ (a, b), PPy (c, d), and 0.75PPy/g-C₃N₄ samples (e, f).

Fig. 4. N₂ adsorption-desorption isotherms of the pure g-C₃N₄ and 0.75PPy/g-C₃N₄ samples (inset: pore-size distribution curves).

Moreover, PPy inhibited the aggregation and controlled the pore distribution of the g-C₃N₄ nanoparticles [40]. The specific surface areas, total pore volume and peak pore size of pure g-C₃N₄ and 0.75PPy/g-C₃N₄ are presented in Table 1. The specific surface area was 18 m² g⁻¹ for 0.75PPy/g-C₃N₄ and 11 m² g⁻¹ for pure g-C₃N₄, which illustrated that PPy introduced a

Table 1

Summary of specific surface areas from BET, total pore volume and peak pore size of the pure g-C₃N₄ and 0.75PPy/g-C₃N₄ samples.

Sample	BET (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Peak pore size (nm)
g-C ₃ N ₄	11	0.08	3.48
0.75PPy/g-C ₃ N ₄	18	0.09	3.50

porous structure and increased the surface area of pure g-C₃N₄. This interesting result agreed well with the SEM observations of the deposited amorphous PPy particles shown in Fig. 3.

3.2. Optical properties

3.2.1. UV-vis DRS and PL analysis

The optical properties of the as-prepared PPy/g-C₃N₄ composites were characterized by UV-vis DRS and PL spectroscopy, as shown in Fig. 5. UV-vis DRS was employed to analyze the intensity of light absorption. In Fig. 5(a), no absorption edge was observed for black PPy because of the absorption over the entire spectrum [32]. For pure g-C₃N₄, the basal absorption edge was at 450 nm, and the absorption intensity over the whole visible light region for the composites gradually increased with increasing the PPy content from 0 to 1 wt%. A slight red-shift in the absorbance was observed, which illustrated the enhanced visible light absorption ability of the composites with the interaction between g-C₃N₄ and PPy semiconductors in the heterojunctions [10]. With a 0.75 wt% PPy loading amount, the absorption edge was at 490 nm, which resulted in a broader absorption than that of pure g-C₃N₄. Based on the above results, PPy served as a photosensitizer with a strong absorption coefficient and caused the photosensitization of g-C₃N₄ [28]. In comparison with the pristine counterpart, the composites modified by PPy were able to enhance the absorption in the visible light region, which could lead to the superior usage of solar light.

Fig. 5(b) shows the PL spectra of the as-synthesized composites under an excitation wavelength of 350 nm, where a lower PL intensity resulted from the higher separation efficiencies of

the photogenerated electron-hole pairs [35]. In general, the fluorescence intensity of the composites decreased when the PPy content was increased from 0 to 1 wt%, as compared with that of g-C₃N₄ alone. Owing to the high conductivity of PPy, 0.75PPy/g-C₃N₄ had the weakest intensity among all of the samples, which suggested that the electrons stimulated from the pure g-C₃N₄ were efficiently transferred by the conjugated structure, thus preventing the recombination of electrons and holes [9]. As a result of the efficient electron separation, a host of electrons could react with the dissolved oxygen on the sample surface to generate superoxide radicals for pollutant degradation [41].

3.2.2. Photocurrent response

To further investigate the separation efficiency of the electron-hole pairs in the composites, the photocurrents generated from the photocatalysts were measured under visible light with several on-off cycles of intermittent irradiation. The photocurrent-time curves of the pure g-C₃N₄ and 0.75PPy/g-C₃N₄ photocatalysts are shown in Fig. 6. The photocurrent was observed to be reproducible and stable. The photocurrent response of 0.75PPy/g-C₃N₄ was constantly more than four-fold higher than that of pure g-C₃N₄. In general, an enhanced photocurrent is widely regarded as the most efficient evidence to demonstrate the separation and diffusion of photogenerated electrons and holes, which are transferred from the inner structure of the photocatalyst to the free charge acceptors on its surface. Furthermore, a high separation efficiency of photoexcited carriers plays a key role in the photocatalytic activity of photocatalysts. Therefore, PPy can effectively suppress electron-hole recombination by intensifying the charge transfer of g-C₃N₄ under visible light irradiation. This result was confirmed by PL spectroscopy, as shown in Fig. 5(b).

3.3. Photoactivity of PPy/g-C₃N₄ composites

3.3.1. Effect of SDBS addition

In this study, the organic acid anion surfactant SDBS was used as the dopant to improve the conductivity of PPy [23].

Fig. 5. UV-vis DRS (a) and PL spectra (b) of the pure g-C₃N₄, PPy and XPPy/g-C₃N₄ (X = 1, 0.75, 0.5, 0.25) samples (inset: band gap determination of pure g-C₃N₄ and 0.75 PPy/g-C₃N₄).

Fig. 6. Photocurrent response curves of pure $\text{g-C}_3\text{N}_4$ and 0.75PPy/ $\text{g-C}_3\text{N}_4$ under visible light irradiation.

Pure PPy possesses a π - π^* double conjugate structure and poor conductivity in a long chain state, thus the introduction of dopants in the polymer structure typically improves the conductivity [24]. However, polymer chains with conjugated structures undergo charge transfer or redox reactions with dopants, so different types of dopants will have different effects on the conductivity mechanism [26]. The visible light photocatalytic activities of the as-prepared samples with different amounts of added SDBS addition were evaluated in the degradation of MB as the target compound. As shown in Fig. 7(a), the composites with 0.1, 0.2, and 0.3 g of SDBS showed higher degradation rates than pristine $\text{g-C}_3\text{N}_4$ after 2 h of visible light irradiation. Particularly, 0.2 g SDBS resulted in a 2.4 times higher degradation efficiency based on the pseudo-first-order model (Fig. 7(b)), which will be discussed later. The composite containing 0.3 g SDBS was burdened with a small amount of pyrrole to form the PPy structure [42], while that containing 0.1 g SDBS was not suitable for the PPy rings. In the reaction, the polymer chains provide electrons and exhibit electropositivity; thus they combine with the anionic surface active agent directly. The addition of SDBS was essential to the internal π - π^* conjugated structure of PPy as well as the effective electron transfer. The

changed energy state of PPy led to the decreased band intensity and increased conductivity. Therefore, with SDBS addition, the primary chain of PPy was changed and easily reacted with the oxygen on the $\text{g-C}_3\text{N}_4$ surface, which resulted in more active substances to facilitate the photodegradation process.

3.3.2. Effect of PPy mass ratio

Next, the visible light photocatalytic activities of the composites with different mass ratios of PPy were evaluated. As shown in Fig. 8(a), the composites exhibited better photoactivities than pure $\text{g-C}_3\text{N}_4$ after 2 h of irradiation with visible light. Moreover, the degradation of MB treated with $\text{g-C}_3\text{N}_4$ with 0.75 wt% PPy reached approximately 99% after 2 h of visible light irradiation. The degradation of MB by 0.75PPy/ $\text{g-C}_3\text{N}_4$ increased by 24% when compared with that with $\text{g-C}_3\text{N}_4$. Moreover, 0.75PPy/ $\text{g-C}_3\text{N}_4$ showed strong adsorption in the dark experiment, mainly because of the increased surface, which was supported by the BET measurements (Fig. 4).

With respect to the reaction kinetics of the MB degradation, a pseudo-first-order model was adopted as shown by the linear fitting of $\ln(C_0/C_t)$ versus t , where k is the apparent pseudo-first-order kinetic constant (min^{-1}) [38]. The kinetic plots and corresponding k values are shown in Fig. 8(b). Apparently, the loaded quantities of PPy greatly influenced the photodegradation rate. The sample with 0.75 wt% PPy exhibited the highest photodegradation efficiency with a k value of 0.03773 min^{-1} , which was 3 times higher than that of pure $\text{g-C}_3\text{N}_4$ (0.01284 min^{-1}). The PPy nanoparticles dispersed on the semiconductor increased the number of single active junctions and enhanced the light absorption of $\text{g-C}_3\text{N}_4$ [23], thereby improving the photodegradation rate and photocatalytic performance.

3.4. Enhanced photodegradation mechanism

According to the aforementioned degradation studies, PPy/ $\text{g-C}_3\text{N}_4$ composites exhibited better photoactivity than $\text{g-C}_3\text{N}_4$. Determining the major oxidative species in the photocatalytic processes may shed light on the photocatalysis mechanism [43]. The ESR spin-trap technique was employed to monitor the reactive species generated upon irradiation of the

Fig. 7. MB degradation efficiency (a) of PPy/ $\text{g-C}_3\text{N}_4$ and first kinetic plots and rate constants k (b) upon addition of SDBS.

Fig. 8. MB degradation efficiency (a), and first-order kinetic plots and rate constants k (b) of PPy/g-C₃N₄ composites with different mass ratios of PPy and g-C₃N₄.

PPy and g-C₃N₄ composite system with DMPO in methanol and in water for superoxide radical ($\cdot\text{O}_2^-$) and hydroxyl radicals ($\cdot\text{OH}$), respectively [44]. The ESR results of pure g-C₃N₄ and 0.75PPy/g-C₃N₄ are shown in Fig. 9. Signals corresponding to DMPO- $\cdot\text{O}_2^-$ were detected in the two samples, as presented in Fig. 9(a). The intensity of the signal of the 0.75PPy/g-C₃N₄ increased slightly after 5 min of irradiation, which confirmed that $\cdot\text{O}_2^-$ serves as an effective radical for pure g-C₃N₄ and PPy/g-C₃N₄ composites photocatalysis. Meanwhile, the DMPO- $\cdot\text{OH}$ signal of 0.75PPy/g-C₃N₄ was observed after 5 min of irradiation (Fig. 9(b)). Moreover, the intensity of the $\cdot\text{OH}$ signal increased considerably after 15 min of irradiation. However, the pure g-C₃N₄ sample showed almost no active signal, which indicated that the addition of PPy enhanced the production of both active radicals by electrons separation through the formation of the composite structure. Moreover, it is illustrated that $\cdot\text{OH}$ cannot be regarded as the active radical for pure g-C₃N₄. Therefore, a reaction mechanism involving both $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ was expected in the photocatalysis process for the composites, as they are the main oxidative species in the PPy/g-C₃N₄ composite systems.

A reasonable degradation mechanism of MB by PPy/g-C₃N₄ catalysts under visible light is depicted in Fig. 10. As an organic semiconductive material, PPy induces the transition of excited electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) because of the highly delocalized π - π^* conjugate structure under visible light [45]. Meanwhile, the conduction band (CB, -2.2 eV) for

Fig. 10. Mechanism of MB degradation with PPy/g-C₃N₄ composites under visible light irradiation.

Fig. 9. DMPO spin-trapping ESR spectra of the pure g-C₃N₄ and 0.75PPy/g-C₃N₄ in a methanol dispersion for $\cdot\text{O}_2^-$ (a) and in an aqueous dispersion for $\cdot\text{OH}$ (b).

electrons (e^-) is formed on the HOMO and the valence band (VB, +0.18 eV) for holes (h^+) is formed on the LUMO in PPy [46]. Moreover, the CB potential of PPy is more negative than that of g-C₃N₄ (CB, -1.3 eV) and thus is regarded as an electron acceptor [47], while PPy acts as an electron transfer channel to rapidly separate electrons injected from the excited state into the CB of pristine g-C₃N₄ [48]. In addition, g-C₃N₄ excited by visible light irradiation generates electron-hole pairs. The photogenerated electrons transit to the CB of g-C₃N₄ to overlap with the electrons from the π^* -orbital of PPy, whereas the photogenerated holes migrate from the g-C₃N₄ VB (+1.4 eV) into the π -orbital of PPy (+0.8 eV) driven by the potential offset [26], which is the main driving force for efficient charge separation and transfer [49]. In the meantime, a steady internal electric field for the redistribution of electrons on one side of the g-C₃N₄ and holes on the opposite side (PPy) has been established, which ensures the effective separation and prolonging of the lifetime of photocarriers. As the photogenerated electrons and holes are spatially separated into two components, the electrons in the CB of g-C₃N₄ could be trapped by O₂ to produce $\cdot O_2^-$ owing to the sufficiently positive potential that is higher than the reduction potential of the O₂/ $\cdot O_2^-$ couple (-0.33 eV vs. NHE) [6,10]. However, the E_{VB} of g-C₃N₄ is lower than the standard redox potential of H₂O/ $\cdot OH$ (+2.38 eV vs. NHE) and $OH^-/\cdot OH$ (+1.99 eV vs. NHE), which indicated that the photogenerated holes of g-C₃N₄ could not oxidize H₂O and OH^- to the active species $\cdot OH$ [7,8,50]. The $\cdot OH$ radicals should be generated by the further reduction of $\cdot O_2^-$ with successive electrons and H^+ . The $\cdot O_2^-$ and $\cdot OH$ radicals can react with MB, which results in the decoloration of dye solution and the formation of CO₂, H₂O, and intermediate products in the degradation process [51]. The major reaction steps under visible light irradiation could be written as follows:

Therefore, the high charge separation and transfer efficiency are important factors for the enhanced photoactivity, which emphasizes the role of PPy in the enhanced photocatalytic ac-

tivity of the composites.

4. Conclusions

PPy/g-C₃N₄ composites were prepared by the *in-situ* polymerization method. Amorphous PPy particles coated on the g-C₃N₄ surface increased the specific surface area, and facilitated the separation of charge carriers, as well as extended the lifetime of electron-hole pairs. The strong absorption coefficient of PPy could strengthen the visible light adsorption of the composites. The $\cdot OH$ and $\cdot O_2^-$ radicals were confirmed to be the main reactive species for the PPy/g-C₃N₄ composites in the photocatalysis process. PPy/g-C₃N₄ exhibited enhanced visible light photocatalytic activity, when compared with g-C₃N₄ owing to the designed heterostructure with band structure matching. The present work provides a new approach for the design of a high-performance g-C₃N₄-based photocatalyst for environmental applications.

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Graphical Abstract

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***In-situ* polymerization for PPy/g-C₃N₄ composites with enhanced visible light photocatalytic performance**

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The degradation efficiency of methylene blue by PPy/g-C₃N₄ composites synthesized by *in-situ* polymerization was three times higher than that of pure g-C₃N₄, where $\cdot OH$ and $\cdot O_2^-$ radicals are the main reactive species.

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原位聚合PPy/g-C₃N₄复合物增强可见光催化性能

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摘要: 近年发展起来的低能耗、高效率的光催化技术为解决环境污染和能源短缺等问题提供了新途径。在众多光催化材料中, 非金属石墨相氮化碳(g-C₃N₄)半导体材料因其化学稳定性和热稳定性优异、能带结构易调控、前驱体价格低廉等特点备受关注。然而, g-C₃N₄的光生电子-空穴对极易复合, 比表面积较小, 不能充分利用太阳光等, 因而其光催化活性较低。目前, 为了提高g-C₃N₄光催化性能, 多采用金属或非金属元素掺杂、与其他物质形成异质结、与其他半导体材料进行共聚合等方式。其中, 共聚合有利于调节g-C₃N₄内部电子结构, 促进g-C₃N₄光生载流子的分离与迁移, 而且具有高度离域 π - π^* 共轭结构的导电聚合物更适合与g-C₃N₄进行共聚合, 从而进一步提高g-C₃N₄的光催化性能。

本文采用原位聚合法制备合成了导电聚吡咯(PPy)与g-C₃N₄的复合材料, 并以10 mg L⁻¹亚甲基蓝(MB)作为目标污染物评价其可见光催化性能。经X射线衍射、扫描电镜、透射电镜、比表面积、紫外-可见光谱等一系列表征分析可知, PPy/g-C₃N₄复合物(002)晶面衍射峰强度较g-C₃N₄减弱, 表明PPy抑制了g-C₃N₄晶型生长, 但未影响其晶型结构。不规则薄片状g-C₃N₄表面均匀地负载有非晶态PPy颗粒, 复合物微观形貌发生变化。PPy与g-C₃N₄共轭芳香环层间堆积形成的介孔、大孔孔径和孔

容积均增加,比表面积增大了 $7\text{ m}^2\text{ g}^{-1}$,使目标污染物能与光催化剂表面活性物质充分接触反应.同时,PPy具有较强吸光系数,对可见光能完全吸收;PPy/g-C₃N₄复合物的可见光吸收边带发生红移,呈现出较g-C₃N₄更强的可见光吸收能力,提高对可见光的利用效率.

光催化降解MB实验结果表明,在可见光(12 W LED灯)照射2 h后,含有0.75 wt% PPy的复合样品0.75PPy/g-C₃N₄表现出最佳光催化活性,MB降解效率为99%;且污染物光催化降解过程符合准一级动力学,反应速率常数(0.03773 min^{-1})约为同条件下g-C₃N₄ (0.01284 min^{-1})的3倍.自由基捕获测试实验表明,g-C₃N₄和0.75PPy/g-C₃N₄均产生了 $\cdot\text{O}_2^-$ 自由基,但后者的 $\cdot\text{O}_2^-$ 信号更强.这是因为PPy也可吸收可见光并激发出电子,该电子转移到g-C₃N₄导带,再与其本身的电子共同与O₂反应生成 $\cdot\text{O}_2^-$.然而只有0.75PPy/g-C₃N₄在光催化过程中产生了 $\cdot\text{OH}$ 自由基,是由于g-C₃N₄的价带(+1.4 eV)较H₂O/ $\cdot\text{OH}$ (+2.38 eV vs. NHE)和OH⁻/ $\cdot\text{OH}$ (+1.99 eV vs. NHE)小,此价带上的h⁺不能与H₂O和OH⁻反应生成 $\cdot\text{OH}$,而是由生成的 $\cdot\text{O}_2^-$ 再与e⁻和H⁺反应产生,即 $\cdot\text{O}_2^- + 2\text{H} + 2\text{e}^-_{\text{CB}} \rightarrow \cdot\text{OH} + \text{OH}^-$.本文最后分析了以 $\cdot\text{O}_2^-$ 和 $\cdot\text{OH}$ 作为主要活性物质的PPy/g-C₃N₄复合物光催化降解污染物的反应机理,PPy具有强导电性,可作为光生电子和空穴的传输通道,抑制其在g-C₃N₄表面的复合.

关键词: PPy/g-C₃N₄复合物; 原位聚合; 可见光催化; 机理; 环境治理

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