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Article

Synergistic photocatalytic effect of porous g-C₃N₄ in a Cr(VI)/4-chlorophenol composite pollution system

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ABSTRACT

The photocatalytic reduction of aqueous Cr(VI) to Cr(III) was preliminarily studied using porous g-C₃N₄ as a photocatalyst under acidic conditions. The observed synergistic photocatalytic effect of porous g-C₃N₄ on a Cr(VI)/4-chlorophenol (4-CP) composite pollution system was further studied under different pH conditions. Compared with single-component photocatalytic systems for Cr(VI) reduction or 4-CP degradation, the Cr(VI) reduction efficiency and 4-CP degradation efficiency were simultaneously improved in the Cr(VI)/4-CP composite pollution system. The synergistic photocatalytic effect in the Cr(VI)/4-CP composite pollution system can be attributed to the accelerated redox reaction between dichromate and 4-CP by electron transfer with porous g-C₃N₄.

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1. Introduction

Multi-component composite pollution systems, such as electroplating wastewater, sludge in polluted water treatment plants, and urban refuse, are widely distributed in nature due to the rapid development of industry and agriculture [1–3]. Since photocatalytic hydrogen production from water splitting was discovered in 1972, photocatalytic technology has been widely used to remove environmental pollution [4–6]. Photo-generated electrons can reduce highly toxic hexavalent chromium (Cr(VI)) in aqueous dichromate (Cr₂O₇²⁻) to low-toxicity trivalent chromium (Cr(III)) under acidic conditions [7]. Furthermore, aqueous organic pollutants can be degraded to carbon dioxide and water by photocatalytic oxidation processes

[8]. However, in the current field of photocatalysis, most research is focused on developing novel photocatalysts and determining their photocatalytic activities in single-component photocatalytic systems, with scientific issues inherent to the photocatalytic reaction itself often ignored [9–11]. In fact, the application of photocatalytic technology to composite pollution systems has great practical significance. A few researchers have attempted to treat multi-component wastewater using photocatalytic processes [12,13]. However, synergistic photocatalytic effects and mechanisms in composite pollution systems have not been clarified.

In recent years, graphitic carbon nitride (g-C₃N₄) has been widely applied as a metal-free semiconductor photocatalyst in the field of environmental photocatalysis due to its advantages,

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including visible-light response, environmental friendliness, and low cost [14–21]. However, the photocatalytic activity of g-C₃N₄ is poor in practical applications due to its bulk layered structure, which limits the surface migration of photogenerated carriers and increases mass transfer resistance in the photocatalytic reaction. Therefore, some researchers have improved the photocatalytic activity of g-C₃N₄ using morphology control strategies, such as constructing carbon nitride nanosheets, hollow spheres, and quantum dots [22–24]. In our previous study, porous g-C₃N₄ was successfully fabricated via a simple precursor pretreatment strategy using melamine co-pretreated with HCl and ethylene glycol (EG) as a raw material [25,26]. The as-prepared porous g-C₃N₄ showed excellent photocatalytic activity owing to the construction of richly porous microstructures.

In this communication, we report a preliminary study of the photocatalytic reduction of aqueous Cr(VI) to Cr(III) using as-prepared g-C₃N₄ or porous g-C₃N₄ as photocatalysts under acidic conditions. We also study the synergistic photocatalytic effect in a composite pollution system of Cr(VI) and 4-chlorophenol (4-CP) using as-prepared porous g-C₃N₄ at different pH values. Compared with single-component photocatalytic systems, the reduction efficiency of Cr(VI) and degradation efficiency of 4-CP were simultaneously improved in the composite system, demonstrating a synergistic photocatalytic effect in the Cr(VI)/4-CP composite pollution system. Finally, we discuss the synergistic photocatalytic mechanism operating in the Cr(VI)/4-CP composite pollution system.

2. Experimental

2.1. Preparation

The photocatalysts were prepared according to our previously reported method [25,26]. Specifically, porous g-C₃N₄ was fabricated via a precursor pretreatment strategy using HCl/EG co-pretreated melamine as a raw material, while g-C₃N₄ was prepared directly using non-pretreated melamine as a precursor. In a typical synthesis, melamine (3 g) was placed into a 100-mL beaker, followed by the addition of HCl (10 mL), EG (10 mL), and water (3 mL). After stirring the white viscous suspension for 1 h at room temperature, the HCl/EG co-pretreated melamine precursor was obtained by washing, centrifugation, and drying. Subsequently, the HCl/EG co-pretreated melamine precursor was transferred to a 10-mL alumina crucible with a cover. The crucible was heated from room temperature to 250 °C in a muffle furnace at a heating rate of 5 °C/min, and then further heated to 550 °C at a rate of 10 °C/min. After maintaining a temperature of 550 °C for 2 h, a sample of yellow porous g-C₃N₄ was obtained after natural cooling and denoted as pg-C₃N₄. For comparison, g-C₃N₄ was prepared by the same method, but using non-pretreated melamine as precursor.

2.2. Characterization

The morphologies of as-prepared g-C₃N₄ and pg-C₃N₄ were characterized by transmission electron microscopy (TEM) us-

ing a JEM-2100F transmission electron microscope at an accelerating voltage of 200 kV. The phase structures of as-prepared g-C₃N₄ and pg-C₃N₄ were analyzed by X-ray diffraction (XRD) using a D8 ADVANCE diffractometer with Cu-K α radiation. The photocatalytic quantum efficiencies of as-prepared g-C₃N₄ and pg-C₃N₄ were studied by photoluminescence (PL) measurements recorded using a HITACHI F-7000 fluorescence spectrophotometer.

2.3. Evaluation

For the photocatalytic tests, a PLS-SXE 300 Xe lamp (300 W, Beijing PerfectLight Co. Ltd., China) with an output wavelength of $\lambda > 320$ nm served as the simulated sunlight source. Photocatalyst (100 mg) and a reaction solution (100 mL) containing K₂Cr₂O₇ (5 mg/L) and 4-CP (20 mg/L) were poured into a 250-mL beaker with a quartz cover. The suspension was ultrasonicated for 10 min and stirred in the dark until adsorption-desorption equilibrium was reached. The light source was then switched on and fixed aliquots of the reaction solution were extracted at predetermined time intervals during irradiation. Changes in Cr(VI) concentration were analyzed using a diphenylcarbazide spectrophotometric method on a Lambda 750S UV/Vis/NIR spectrometer at $\lambda = 540$ nm. The total Cr concentration was determined using a ContrAA700 graphite furnace atom adsorption spectrometer. The Cr(III) concentration was calculated by subtracting the Cr(VI) content from the total Cr content. Changes in 4-CP concentration were analyzed using an Agilent 1100 series high-performance liquid chromatography system with a C₁₈ column and a UV detector ($\lambda = 277$ nm). Acetonitrile/water (60/40, v/v) was used as the mobile phase at a flow rate of 1.0 mL/min. Variations in the UV-vis adsorption spectra of Cr(VI) and 4-CP under simulated sunlight irradiation were detected using a Lambda 750S UV/Vis/NIR spectrometer. For comparison, photocatalytic tests were also performed on a single-component photocatalytic systems containing either K₂Cr₂O₇ (5 mg/L) or 4-CP (20 mg/L).

3. Results and discussion

The morphologies of as-prepared g-C₃N₄ and pg-C₃N₄ were studied using TEM (Fig. 1). As shown in Fig. 1(a), g-C₃N₄ exhibited a bulk layered graphite-like structure originating from melamine polycondensation under high temperature. As shown in Fig. 1(b), pg-C₃N₄ with a three-dimensional pore geometry was successfully fabricated using HCl/EG co-pretreated melamine as the precursor. Phase structures of as-prepared g-C₃N₄ and pg-C₃N₄ were obtained by XRD analysis (Fig. 2). The results showed that g-C₃N₄ exhibited a typical (002) interlayer stacking peak at 27.5°, corresponding to an interlayer distance of $d = 0.33$ nm, while the (100) peak at 12.9° represented an in-plane structural packing motif with a period of 0.675 nm. The weaker diffraction intensity of the (002) peak in pg-C₃N₄ compared with that in g-C₃N₄ was attributed to the reduced amount of layered structure resulting from the construction of a porous microstructure. The photocatalytic quantum efficiencies of as-prepared g-C₃N₄ and pg-C₃N₄ were studied using PL

Fig. 1. TEM images of as-prepared g-C₃N₄ (a) and pg-C₃N₄ (b).

Fig. 2. XRD patterns of as-prepared g-C₃N₄ and pg-C₃N₄.

measurements (Fig. 3). As shown in Fig. 3, g-C₃N₄ exhibited a broad fluorescence emission peak in the range 400–600 nm with an excitation wavelength of 330 nm and an operating voltage of 400 V. This finding suggested that photoinduced electron-hole (e^-h^+) pairs were generated and recombined within g-C₃N₄. Compared with g-C₃N₄, the decreased PL intensity of pg-C₃N₄ indicated that efficient separation and transportation of photogenerated carriers were realized after formation of the porous microstructure.

The photocatalytic reduction of aqueous Cr(VI) to Cr(III) was studied preliminarily using as-prepared g-C₃N₄ and

Fig. 3. PL spectra of as-prepared g-C₃N₄ and pg-C₃N₄.

pg-C₃N₄ under simulated sunlight irradiation. The reaction solution pH was adjusted to 3 with dilute H₂SO₄. As shown in Fig. 4(a), the blank test result showed that aqueous Cr(VI) could not be reduced to Cr(III) in the absence of photogenerated electrons. As clearly shown in Fig. 4(a), the reduction rate of Cr(VI) and generation rate of Cr(III) were simultaneously increased using pg-C₃N₄ compared with using g-C₃N₄. This result indicated that the photocatalytic activity of pg-C₃N₄ was better than that of g-C₃N₄ because the construction of porous microstructures facilitated the surface migration of photogenerated carriers and decreased mass transfer resistance in the photocatalytic reaction. Fig. 4(b) shows variations in the characteristic absorption of Cr(VI) under simulated sunlight irradiation using pg-C₃N₄ as a photocatalyst. The characteristic absorption of Cr(VI) gradually decreased with increasing irradiation time, which was consistent with the photocatalytic activity curve of pg-C₃N₄, as shown in Fig. 4(a).

In the Cr(VI)/4-CP composite pollution system with pH adjusted to 3 using dilute H₂SO₄, Cr(VI) reduction and 4-CP degradation were simultaneously carried out under simulated sunlight irradiation and the system demonstrated a synergistic photocatalytic effect. As shown in Fig. 5(a), the blank test result

Fig. 4. Photocatalytic activity curves of as-prepared g-C₃N₄ and pg-C₃N₄ toward aqueous Cr(VI) reduction to Cr(III) (a). UV-vis adsorption spectra of photocatalytic reaction solution during the reduction of Cr(VI) to Cr(III) process over pg-C₃N₄ as a photocatalyst (b). Reaction conditions: $M(\text{catalyst}) = 100 \text{ mg}$, $V_0(\text{Cr(VI)}) = 100 \text{ mL}$, $C_0(\text{Cr(VI)}) = 10 \text{ mg/L}$, $\text{pH} = 3$.

showed that both Cr(VI) and 4-CP concentrations hardly decreased in the absence of photocatalyst. This result indicated that the redox reaction between Cr(VI) and 4-CP was difficult to carry out in dilute solution. As clearly shown in Fig. 5(a), in comparison with single-component photocatalytic systems adjusted to pH 3 using dilute H_2SO_4 , both the Cr(VI) reduction efficiency and 4-CP degradation efficiency were significantly improved in the Cr(VI)/4-CP composite pollution system. This result implied that a new photocatalytic reaction was occurring in addition to the individual photocatalytic reduction of Cr(VI) and photocatalytic oxidation of 4-CP that generated a synergistic photocatalytic effect in the Cr(VI)/4-CP composite pollution system. Fig. 5(b) shows variations in the characteristic absorption of Cr(VI) and 4-CP under simulated sunlight irradiation using pg- C_3N_4 as a photocatalyst. The characteristic absorptions of Cr(VI) and 4-CP were reduced by prolonging the irradiation time to 30 min, and the characteristic absorptions of Cr(VI) and 4-CP were hardly observed after 60 min of simulated sunlight irradiation. This result was consistent with the photocatalytic activity curves of the Cr(VI)/4-CP composite pollution system, as shown in Fig. 5(a).

In the Cr(VI)/4-CP composite pollution system without adjusted pH, Cr(VI) reduction and 4-CP degradation were also

performed simultaneously under simulated sunlight irradiation, with a synergistic photocatalytic effect identified in the system. As shown in Fig. 6(a), almost no redox reaction occurred between Cr(VI) and 4-CP in the blank test without photocatalyst under simulated sunlight irradiation. In the Cr(VI) reduction single-component photocatalytic system without adjusted pH, aqueous Cr(VI) could not be reduced by photo-generated electrons under neutral conditions due to the high electron cloud density of the oxygen atoms. In the 4-CP degradation single-component photocatalytic system without adjusted pH, aqueous 4-CP was degraded smoothly by the photocatalytic oxidation process. In the Cr(VI)/4-CP composite pollution system without adjusted pH, both the Cr(VI) reduction efficiency and 4-CP degradation efficiency were improved compared with the respective single-component photocatalytic systems, further demonstrating that a synergistic photocatalytic effect existed in the Cr(VI)/4-CP composite pollution system. Fig. 6(b) shows variations in the characteristic absorption of Cr(VI) and 4-CP under simulated sunlight irradiation using pg- C_3N_4 as a photocatalyst. The characteristic absorptions of Cr(VI) and 4-CP gradually decreased with prolonged irradiation time, which was consistent with the photocatalytic activity curves of the Cr(VI)/4-CP composite pollution system, as

Fig. 5. Photocatalytic activity curves (a) and UV-vis adsorption spectra (b) in the Cr(VI) and 4-CP composite pollution system with adjusting pH to 3. Reaction conditions: $M(\text{pg-C}_3\text{N}_4) = 100 \text{ mg}$, $V_0(\text{Cr(VI)+4-CP}) = 100 \text{ mL}$, $C_0(\text{Cr(VI)}) = 10 \text{ mg/L}$, $C_0(4\text{-CP}) = 20 \text{ mg/L}$.

Fig. 6. Photocatalytic activity curves (a) and UV-vis adsorption spectra (b) in the Cr(VI) and 4-CP composite pollution system without adjusting pH. Reaction conditions: $M(\text{pg-C}_3\text{N}_4) = 100 \text{ mg}$, $V_0(\text{Cr(VI)+4-CP}) = 100 \text{ mL}$, $C_0(\text{Cr(VI)}) = 10 \text{ mg/L}$, $C_0(4\text{-CP}) = 20 \text{ mg/L}$.

shown in Fig. 6(a).

The above simultaneous Cr(VI) reduction with 4-CP degradation reaction was repeated four times to evaluate the stability of the as-prepared pg-C₃N₄ catalyst in the Cr(VI)/4-CP composite pollution system. After the first catalytic run, the catalyst was recovered by centrifugation and washed with water at room temperature. The recovered catalyst was used for subsequent catalytic runs under the same experimental conditions. As shown in Fig. 7(a) and (b), as-prepared pg-C₃N₄ exhibited high stability in the Cr(VI)/4-CP composite pollution system and maintained similar reactivity after four catalytic cycles. The gradual decrease in photocatalytic activity could be attributed to loss of photocatalyst during the recovery process.

In our previous study, we showed that photocatalytic reactions involved in degradation, hydrogen evolution, and simultaneous hydrogen evolution/organic pollutant degradation systems are redox processes, with the photocatalyst acting as an electron transfer medium [27,28]. Specifically, oxygen acts as an oxidizing agent and organic pollutants act as reducing agents in photocatalytic degradation systems, water acts as an oxidizing agent and electron donors act as reducing agents in photocatalytic hydrogen evolution systems, and water acts as

an oxidizing agent and organic pollutants act as reducing agents in simultaneous hydrogen evolution/organic pollutant degradation photocatalytic systems. In the current Cr(VI) reduction single-component photocatalytic system, the electron cloud density of the oxygen atoms in Cr₂O₇²⁻ was decreased under acidic conditions, and Cr₂O₇²⁻ itself underwent redox reactions by electron transfer with the photocatalyst (Scheme 1). Therefore, Cr(VI) reduction by photogenerated electrons proceeded smoothly under acidic conditions (Fig. 4(a)). Conversely, Cr(VI) was not reduced by photogenerated electrons under neutral conditions due to the high electron cloud density of oxygen atoms in Cr₂O₇²⁻ (Scheme 1 and Fig. 6(a)). In the 4-CP degradation single-component photocatalytic system, the redox reaction between 4-CP and dissolved oxygen occurred by electron transfer with the photocatalyst (Scheme 1). Therefore, hydrogen ions had little effect on the 4-CP degradation efficiency (Figs. 5(a) and 6(a)). Furthermore, the redox reaction between Cr₂O₇²⁻ and 4-CP was switched on by electron transfer with the photocatalyst in the Cr(VI)/4-CP composite pollution system (Scheme 1). Therefore, compared with the single-component photocatalytic systems, both the Cr(VI) reduction efficiency and 4-CP degradation efficiency were improved in the Cr(VI)/4-CP composite pollution system (Figs. 5(a) and 6(a)). This showed that a synergistic photocatalytic effect existed in the Cr(VI)/4-CP composite pollution system. In general, Cr₂O₇²⁻ showed a strong oxidizing ability under acidic conditions because the electron cloud density of oxygen atoms in Cr₂O₇²⁻ was decreased by hydrogen ions. However, Cr₂O₇²⁻ hardly exhibited oxidative properties under neutral conditions due to the high electron cloud density of oxygen atoms in Cr₂O₇²⁻ [29,30]. In the Cr(VI)/4-CP composite pollution system with pH adjusted to 3 using dilute H₂SO₄, the redox reaction between Cr₂O₇²⁻ and 4-CP was easily carried out by electron transfer with pg-C₃N₄ in the presence of a large amount of hydrogen ions owing to the low electron cloud density of oxygen atoms in the Cr₂O₇²⁻. Therefore, an obvious synergistic photocatalytic effect was observed in the Cr(VI)/4-CP composite pollution system with pH adjusted to 3 by dilute H₂SO₄ (Fig. 5(a)). However, in the Cr(VI)/4-CP composite pollution system without adjusted pH, the electron cloud density of oxygen atoms in Cr₂O₇²⁻ was only be reduced by hydrogen ions derived from 4-CP. Therefore, the redox reaction between Cr₂O₇²⁻ and 4-CP was inhibited in the Cr(VI)/4-CP composite pollution system without adjusting the pH (Fig. 6(a)).

4. Conclusions

Compared with g-C₃N₄, the photocatalytic activity of pg-C₃N₄ was significantly increased in the reduction of Cr(VI) owing to the construction of porous microstructures. In the Cr(VI)/4-CP composite pollution system, both the Cr(VI) reduction efficiency and 4-CP degradation efficiency were improved with respect to the single-component photocatalytic systems regardless of whether the pH was adjusted, demonstrating that a synergistic photocatalytic effect existed in the Cr(VI)/4-CP composite pollution system. The synergistic photocatalytic effect in the Cr(VI)/4-CP composite pollution system was attributed to the

Fig. 7. Recyclability of pg-C₃N₄ in the Cr(VI) and 4-CP composite pollution system with adjusting pH to 3 (a) and without adjusting pH (b).

Scheme 1. The photocatalytic reaction mechanisms in the Cr(VI) reduction, 4-CP degradation, and simultaneous reduction of Cr(VI) with 4-CP degradation photocatalytic systems.

accelerated redox reaction between $\text{Cr}_2\text{O}_7^{2-}$ and 4-CP via electron transfer with pg- C_3N_4 . In the Cr(VI)/4-CP composite pollution system adjusted to pH = 3 with dilute H_2SO_4 , the redox reaction between $\text{Cr}_2\text{O}_7^{2-}$ and 4-CP was easily performed via electron transfer with pg- C_3N_4 because of the low electron cloud density of oxygen atoms in $\text{Cr}_2\text{O}_7^{2-}$. Therefore, an obvious synergistic photocatalytic effect was observed in the Cr(VI)/4-CP composite pollution system when adjusted to pH = 3.

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Graphical Abstract

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The synergistic photocatalytic effect of pg-C₃N₄ was studied under different pH conditions. The Cr(VI) reduction and 4-CP degradation efficiencies were both improved compared with their respective single-component photocatalytic systems. This synergistic photocatalytic effect was attributed to the accelerated redox reaction between Cr₂O₇²⁻ and 4-CP due to electron transfer with pg-C₃N₄.

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在Cr(VI)和4-氯酚复合污染系统中多孔石墨相氮化碳的协同光催化效应

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摘要: 随着工农业的迅速发展, 多组分复合污染系统广泛分布于自然环境中, 例如电镀废水、污水处理厂污泥、城市生活垃圾等。自1972年光催化裂解水产氢被发现以来, 光催化技术已被广泛应用于解决环境污染问题。一方面, 光生电子在酸性条件下能将重铬酸根(Cr₂O₇²⁻)中高毒性的Cr(VI)还原成低毒性的Cr(III)。另一方面, 水中有机污染物通过光催化氧化过程可被降解为二氧化碳和水。然而在目前的光催化领域, 大部分研究者专注于新型光催化剂的开发, 并在单组份光催化系统中测试所开发材料的光催化活性, 而忽视了蕴藏在光催化反应本身中的科学问题。事实上, 将光催化技术应用于复合污染系统具有非常大的现实意义。少数研究者试图通过光催化过程处理多组分废水。然而, 在复合污染系统中的协同光催化效应和机理尚未明确。

近几年, 基于可见光响应、环境友好、成本低等优点, 作为一种不含金属的半导体光催化剂, 石墨相氮化碳(g-C₃N₄)已被广泛应用于环境光催化领域。然而在实际应用中, g-C₃N₄的光催化活性却较差, 因为聚集态层状结构不但限制了光生载流子的表面迁移, 而且还增加了光催化反应的传质阻力。因此, 人们尝试形貌控制策略来提高g-C₃N₄的光催化活性, 例如氮化碳纳米片、空心球、量子点的构建。在前期工作中, 我们通过一种简单的前驱体预处理策略使用盐酸和乙二醇共处理的三聚氰胺作原料成功制备出了多孔石墨相氮化碳(pg-C₃N₄), 因其具有丰富的多孔微观结构而表现出了卓越的光催化活性。

本文初步研究了在酸性条件下使用所制备g-C₃N₄或pg-C₃N₄光催化还原水中Cr(VI)成Cr(III)的反应. 然后在不同pH条件下进一步研究了在Cr(VI)和4-氯酚(4-CP)复合污染系统中的协同光催化效应. 结果发现, 与单组分光催化系统相比, 在Cr(VI)和4-CP复合污染系统中Cr(VI)的还原效率和4-CP的降解效率同时提高, 即在Cr(VI)和4-CP复合污染系统中存在协同光催化效应. 最后讨论了在Cr(VI)和4-CP复合污染系统中的协同光催化效应可归因于pg-C₃N₄的电子转移作用加速了Cr₂O₇²⁻和4-CP之间的氧化还原反应. 在用稀H₂SO₄调节pH至3的Cr(VI)和4-CP复合污染系统中, 由于Cr₂O₇²⁻中氧原子的电子云密度较低, 因此Cr₂O₇²⁻和4-CP之间的氧化还原反应通过pg-C₃N₄的电子转移作用易于进行, 因而表现出明显的协同光催化效应.

关键词: 复合污染; 协同光催化作用; 多孔石墨相氮化碳; Cr(VI); 4-氯酚

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