

Enhanced Visible Light Photocatalytic Performance of $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ Composites Assisted by Hydrogen Peroxide

Quan-Liang Chen, Yi-Ling Liu

Abstract—Different loading rates of composite photocatalysts $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ were prepared by in situ precipitation method and were characterized by IR and XRD spectroscopies. Their photocatalytic performances were evaluated by the degradation of RhB under visible light irradiation. $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ composites assisted by H_2O_2 shows higher photocatalytic performance than that of Fe_3O_4 or $\text{g-C}_3\text{N}_4$. As the dosage rate of Fe_3O_4 increases, the degradation rate is slightly increased. The $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4(0.1:1)$ composite has the best photocatalytic performance. It is inferred that the introduction of Fe_3O_4 is beneficial for the separation of photogenerated electrons and holes on the surface of the catalyst.

Index Terms—carbon nitride; hydrogen peroxide; RhB; composite photocatalyst

I. INTRODUCTION

Energy shortage and environmental pollution have become the restrictive factors for the economic development of various countries. Semiconductor photocatalytic technology is believed as the potential way to solve the problems due to its potential use in solar hydrogen production, environmental protection and water treatment. In the semiconductor photocatalysis technology, high photocatalytic efficiency is the precondition of its practical application. The photocatalytic efficiency is related to the composition and structure of semiconductor materials. The ideal photocatalyst should have broad spectrum absorption, good stability, high charge separation efficiency, strong redox ability and high specific surface area. Therefore, how to control the microstructure of photocatalysts and improve its photocatalytic efficiency of semiconductors is one of the most important goals of semiconductor photocatalytic technology research.

Graphite phase carbon nitride ($\text{g-C}_3\text{N}_4$) has become a hot topic in the field of photocatalysis because of its easy preparation, non-toxic, cheap, excellent thermal stability and chemical stability. In addition, $\text{g-C}_3\text{N}_4$ shows high activity in the field of heterogeneous catalysis, catalytic organic reaction and so on. However, the photocatalytic activity of $\text{g-C}_3\text{N}_4$ is limited by the small surface area, fast carrier recombination and low light quantum efficiency. The semiconductor physical composition is an effective way to improve the photocatalytic activity.

In this paper, $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ composite photocatalysts were synthesized by in situ precipitation method. Their photocatalytic performance for the degradation of rhodamine b (RhB) as a model pollutant was studied.

II. EXPERIMENT

A. Materials and instrumentation

Melamine, hydrogen peroxide, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, Rhodamine B and other materials were purchased from Sigma. They were analytical reagents and used without further purification. FT-IR spectra were acquired in the range of $400\text{-}4000\text{ cm}^{-1}$ with NICOLET 380 FT-IR spectrometer using KBr and sample mixture pellets. Electronic spectra were recorded in water on a UV 1800 spectrophotometer. X-ray diffraction (XRD) measurements were obtained on a Bruker D8 Advance diffractometer with $\text{Cu K}\alpha$ radiation. pH value was determined by PHB-8 digital pH meter.

B. Preparation of photocatalysts

Preparation of $\text{g-C}_3\text{N}_4$. $\text{g-C}_3\text{N}_4$ was prepared by directly calcinating 10 g of melamine in a muffle furnace at $550\text{ }^\circ\text{C}$ for 2.5 h with ramping rate of $2\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. After cooling to room temperature, the yellow powders were washed with deionized water and ethanol several times to remove any soluble impurities. After drying under vacuum at $80\text{ }^\circ\text{C}$ overnight, the product $\text{g-C}_3\text{N}_4$ was obtained by grinding for half hour.

Preparation of $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ composite catalysts. $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ composite catalysts were prepared by in situ precipitation method. 1 g $\text{g-C}_3\text{N}_4$ was dispersed in a solution of ethanol and water with the volume ratio of 1:2. The mixture was ultrasonicated for 90 min at ambient temperature. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.335 g, 8.64 mmol) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.859 g, 4.32 mmol) were dissolved in 300 mL water with constant stirring. This solution was then added slowly to the suspension of $\text{g-C}_3\text{N}_4$ with the speed of $10\text{ mL}\cdot\text{min}^{-1}$. The pH value of the mixture was adjusted to 10 ~ 11 by adding dilute ammonium solution. After that, the mixture was heated at $80\text{ }^\circ\text{C}$ for 1 h with constant stirring. After cooling to room temperature, the product was washed with deionized water and ethanol several times to remove any soluble impurities. After drying under vacuum at $60\text{ }^\circ\text{C}$ overnight, the product named as $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4\text{-}1:1$ was obtained by grinding for half hour. The other composite photocatalysts with 0.1, 0.2, 0.5, 0.7 wt% Fe_3O_4 were prepared by the same method and named as

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Fe₃O₄/g-C₃N₄(0.1:1), Fe₃O₄/g-C₃N₄(0.2:1),
Fe₃O₄/g-C₃N₄(0.5:1), Fe₃O₄/g-C₃N₄(0.7:1), respectively.

C. Photocatalytic reactivity

The photocatalytic performances of the as-prepared Fe₃O₄/g-C₃N₄ were evaluated by the degradation of RhB under visible light irradiation from a 300W Xe lamp with a 420 nm cutoff filter. Cooling water was circulated between two walls to cool down the lamp during the radiation. The samples were kept at 20 cm from the lamp. In each experiment, 25 mg of photocatalyst was dispersed in 50 mL aqueous solution of RhB (10 mg/L). Prior to irradiation, the suspension was magnetically stirred in the darkness for 30 min to obtain the absorption-desorption equilibrium. During the photocatalytic reaction, 3 mL of RhB solution with catalyst was sampled at the certain time intervals and centrifuged to remove the solid photocatalyst. The concentration of RhB was determined by means of a UV-vis spectrophotometer at a wavelength of 550 nm.

III. RESULTS AND DISCUSSION

IR spectra of g-C₃N₄, Fe₃O₄ and Fe₃O₄/g-C₃N₄ composites were shown in Figure 1. In the spectrum of g-C₃N₄, it shows broad peaks in the region of 3000-3400 cm⁻¹ corresponding to stretching vibration modes of -NH₂, -NH- groups. Peaks in the region of 1240-1643 cm⁻¹ are due to C-N conjugated heterocyclic structures of g-C₃N₄. The intense band at 809 cm⁻¹ is the ring breath vibration showing a well-ordered heptazine with deprotonating. The spectrum of Fe₃O₄ shows intense band at 577 cm⁻¹ consistent with that reported in the literature. From the spectra of Fe₃O₄/g-C₃N₄ composites, it can be clearly seen that they possess the characteristic peaks of Fe₃O₄ and g-C₃N₄, indicating that the composite catalysts is the combination of g-C₃N₄ and Fe₃O₄.

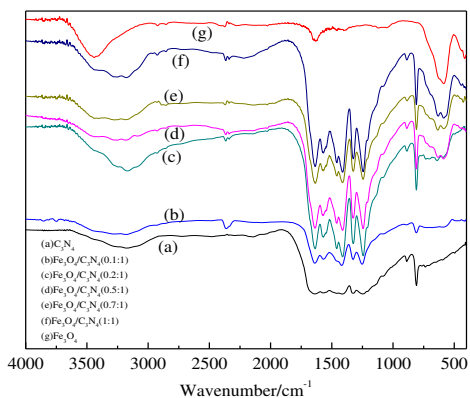


Fig.1 IR spectra of g-C₃N₄, Fe₃O₄ and Fe₃O₄/g-C₃N₄ composite catalysts.

As shown in Figure 2, the XRD spectrum of g-C₃N₄ has two strong peaks at 13.1° and 27.5°, corresponding to the (100) and (002) diffraction planes of g-C₃N₄ respectively. The strong peak at 27.5° is related to the interlayer reflection of the graphitic-like structure in g-C₃N₄. Another small peak at 13.1° corresponds to in-planar repeat tris-triazine units in g-C₃N₄. The spectrum of g-C₃N₄ is consistent with other XRD spectrum of g-C₃N₄ reported in the literature. The spectrum indicates the successful transformation of

graphitic phase from melamine. The XRD spectrum of Fe₃O₄ shows peaks at 30.1°, 35.6°, 43.2°, 53.6°, 57.1° and 62.7°. They corresponds to the (220), (311), (400), (466), (511), (440) diffraction respectively. As for the XRD patterns of Fe₃O₄/g-C₃N₄ composites, they shows the characteristic peaks of Fe₃O₄ and g-C₃N₄, indicating the successful composition of Fe₃O₄ and g-C₃N₄. When the doping amount of Fe₃O₄ is increasing, the characteristic peak of Fe₃O₄ is more obvious.

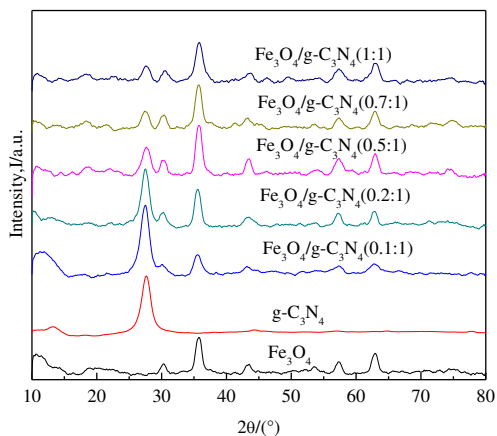


Fig.2 XRD patterns of g-C₃N₄, Fe₃O₄ and different Fe₃O₄/g-C₃N₄ composites.

The photocatalytic performance of pure g-C₃N₄, pure Fe₃O₄ and Fe₃O₄/g-C₃N₄ composites were studied for the degradation of RhB under visible light irradiation. As shown in Figure 3, only 9.5% of RhB was removed by pure g-C₃N₄ under 120 min irradiation. The photocatalytic performance of pure Fe₃O₄ and Fe₃O₄/g-C₃N₄(0.1:1) are a little better, 15.5% and 18.0% of RhB were degraded. If in the presence of H₂O₂, Fe₃O₄ shows better photocatalytic performance. The degradation rate of RhB reaches 52.7%. However, under the same condition, Fe₃O₄/g-C₃N₄(0.1:1) composite has the highest degradation efficiency, 84.0% of RhB was removed under 2 h irradiation. The result indicates the composition of Fe₃O₄ and g-C₃N₄ improves the photocatalytic performance assisted by H₂O₂. It can be inferred that the introduction of Fe₃O₄ improves the optical absorption properties of C₃N₄, which is beneficial to the separation of photogenerated electrons and holes on the surface.

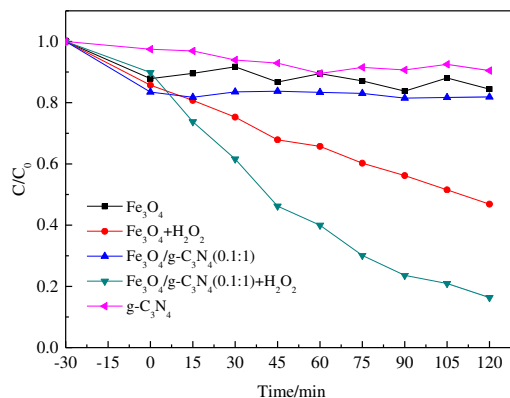


Fig.3 Photocatalytic performance of RhB by g-C₃N₄, Fe₃O₄ and Fe₃O₄/g-C₃N₄ composite in the presence H₂O₂.

The photocatalytic performance of different $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ composites were evaluated in the presence of H_2O_2 . As shown in Figure 4, the degradation rates of RhB by different $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ composites are not so far different. In general, as the dosage rate of Fe_3O_4 increases, the degradation rate is slightly increased. The $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4(0.1:1)$ composite has the best photocatalytic performance.

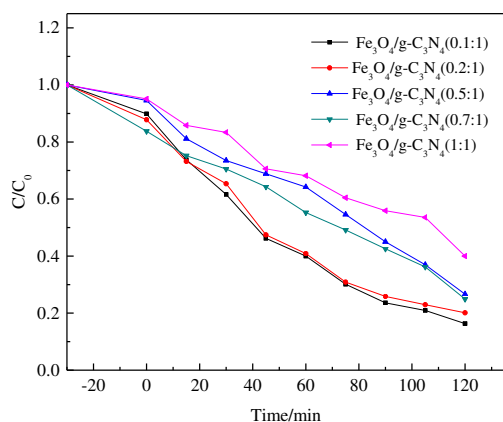


Fig.4 Photocatalytic performance of different $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ composite catalysts assisted by H_2O_2 .

IV. CONCLUSION

In this paper, $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ composite photocatalysts were prepared and characterized by IR and XRD spectroscopy. It can be clearly seen that the IR and XRD spectra of $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ possess the characteristic peaks of Fe_3O_4 and $\text{g-C}_3\text{N}_4$, indicating the good composition of Fe_3O_4 and $\text{g-C}_3\text{N}_4$. The photocatalytic reactivity test showed that $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ assisted by H_2O_2 has higher catalytic efficiency than that of pure Fe_3O_4 or $\text{g-C}_3\text{N}_4$. The study on the effect of pH and temperature on the photocatalytic performance is still ongoing.

ACKNOWLEDGMENT

This research was supported by the Fundamental Research Funds for the Central Universities (No. 2017NZYQN10) in Southwest Minzu University.

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