

Co₃O₄ Modified C₃N₄ Catalysts with Enhanced Photodegradation Performance toward Methyl Blue

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Abstract—Different loading rates of photocatalysts Co₃O₄/C₃N₄ were prepared by calcination method. Their photocatalytic performances were evaluated by the degradation of methyl blue under visible light irradiation. The results show that the introduction of Co₃O₄ significantly improves the optical absorption properties of C₃N₄, which is beneficial to the separation of photogenerated electrons and holes on the surface of catalyst. The prepared Co₃O₄/C₃N₄ for visible photocatalytic degradation of methyl blue has higher catalytic efficiency than that of pure C₃N₄ or pure Co₃O₄. The best cobalt loading rate was 30% when the concentration of methylene blue was 40 mg/L. Recycling rate of 30% Co₃O₄/C₃N₄ composite catalyst was studied. After 4 cycles, the degradation rate was only slightly decreased from 86.8% to 82.8%, indicating the catalyst with good photostability and repeatability.

Index Terms—carbon nitride; photocatalyst; methyl blue; energy gap

I. INTRODUCTION

Environmental pollution and energy crisis has caused more and more attention nowadays. Photocatalytic technology, as a new catalytic technology, can not only decompose water to hydrogen, but also can convert solar energy into electrical energy and chemical energy. It is potential to solve the problem of environmental pollution and energy shortage [1-3]. However, most reported photocatalysts have similar problems: (1) The energy gap is too wide, only in response to the UV region and low rate of utilization of solar energy in 47% visible light; (2) Electric potential of the valence and conduction band is difficult to meet the needs of electric potential in a variety of catalytic reactions; (3) Light induced electron and hole are easy to recombine leading to low quantum efficiency [4-6].

Carbon nitride (C₃N₄) is a new kind of nonmetal photocatalyst. The material is cheap, environmentally friendly, easy to be prepared by a variety of cheap raw materials [7,8]. Compared with other semiconductors, C₃N₄ has wider energy gap with 2.7 eV to absorb visible light. However, its high electron-hole recombination rate leads to low quantum efficiency [9-14]. In order to improve the photocatalytic activity of C₃N₄, researchers have tried a variety of modification methods. Physical modification is one of the most convenient ways. C₃N₄ and composite material is not a simple physical mixture, while full contact will make the formation of heterojunction [15-18]. Because of the difference of the two conduction bands and valence bands, electron or hole produced by C₃N₄ transfers to conduction or valence band of the complex lowers the combination rate of electron and hole. Another method is using a template for the synthesis of different structures of

nano porous C₃N₄. Non-metal doping and metal doping on C₃N₄ to improve its photodegradation performance is also one method. The specific surface area and microstructure of C₃N₄ also affects its photocatalytic activity. Therefore, the improvement of the photocatalytic performance of C₃N₄ can be realized by the porous and low dimension of C₃N₄ microstructure. Due to the higher surface area of C₃N₄, such as porous, nano particles, nanorods and nano thin films, the photocatalytic performance is improved obviously. Until now, some semiconductor materials, such as WO₃/C₃N₄, TiO₂/C₃N₄, and ZnO₂/C₃N₄ have been reported [19-22]. These composites have higher photocatalytic activity than that of pure C₃N₄ or pure metal oxides.

In this paper, Co₃O₄/C₃N₄ composite photocatalysts were synthesized by calcination method. Their photocatalytic degradation ability of methyl blue as a model pollutant was studied.

II. EXPERIMENT

A. Materials and instrumentation

Melamine, methyl blue, Ludox HS40, cobalt nitrate, ethanol were purchased from Sigma. All chemicals were analytical reagents and used without further purification. pH value was determined by PHB-8 digital pH meter. FTIR spectra were acquired in the range of 400-4000 cm⁻¹ with NICOLET 380 FT-IR spectrometer using KBr and sample mixture pellets.

B. Preparation of Co₃O₄/C₃N₄

Preparation of C₃N₄. Melamine (15.15 g) and silica sol (19.75 g Ludox HS40) were mixed and dissolved in water. The solution were then transferred to an oven to be dried at 80 °C. After that, the solid was calcined in a muffle furnace at 550 °C for 2.5 hours. After cooling to room temperature, the solid was then collected and dispersed in NH₄HF₂ solution to remove SiO₂. The yellow product C₃N₄ was washed with ethanol and water, then was dried in an oven at 70 °C.

Preparation of Co₃O₄. Co₃O₄ powder was prepared by direct heating Co(NO₃)₂·6H₂O at 300 °C in a muffle furnace for 2 h in an alumina crucible with a cover at a heating rate of 20 °C/min.

Preparation of Co₃O₄/C₃N₄. C₃N₄ (1.0 g) was added in 5 mL water and then was treated in an ultrasonic cleaner for 0.5 hours. 0.57 g Co(NO₃)₂·6H₂O was added to the solution with constant stirring. After the solution dried in an 80 °C oven, the solid was calcined in a muffle furnace at 550 °C for 2.5 h. The solid was collected and washed with ethanol and water. The product was dried in an oven at 70 °C to get Co₃O₄/C₃N₄ with 10% mass ratio, which was named as 10% Co₃O₄/C₃N₄. The catalysts with other mass ratios were

prepared in the similar procedure.

C. Photodegradation reaction

The photocatalytic performances of the as-prepared C₃O₄/C₃N₄ were evaluated by the degradation of methyl blue 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, 15 mg of photocatalyst was dispersed in 60 mL aqueous solution of methyl blue (40 mg/L) in an ultrasound generator for 5min. Prior to irradiation, the suspension was magnetically stirred in the darkness for 20 min to obtain the absorption-desorption equilibrium. During the photodegradation reaction, 3 mL of methyl blue solution with catalyst was sampled at the certain time intervals and centrifuged to remove the solid photocatalyst. The concentration of methyl blue was determined by means of a UV-vis spectrophotometer. The obtained results revealed negligible change in the initial concentration of the pollutants.

III. RESULTS AND DISCUSSION

IR spectra of pure C₃N₄, pure Co₃O₄ and 30% Co₃O₄/C₃N₄ catalyst were shown in Figure 1. The spectrum of C₃N₄ shows broad peaks between 3100 and 3400 cm⁻¹ corresponding to -NH₂, -NH- groups. Peaks in the region of 1240-1643 cm⁻¹ are due to C-N conjugated heterocyclic structures. The intense band at 808 cm⁻¹ is the ring breath vibration showing a well-ordered heptazine with deprotonating. The spectrum of C₃O₄ shows intense band at 550 and 600 cm⁻¹. From the spectrum of 30% Co₃O₄/C₃N₄, it can be clearly seen that the 30% Co₃O₄/C₃N₄ possess the characteristic peaks of Co₃O₄ and C₃N₄, indicating that the catalyst is indeed formed by the combination of C₃N₄ and Co₃O₄.

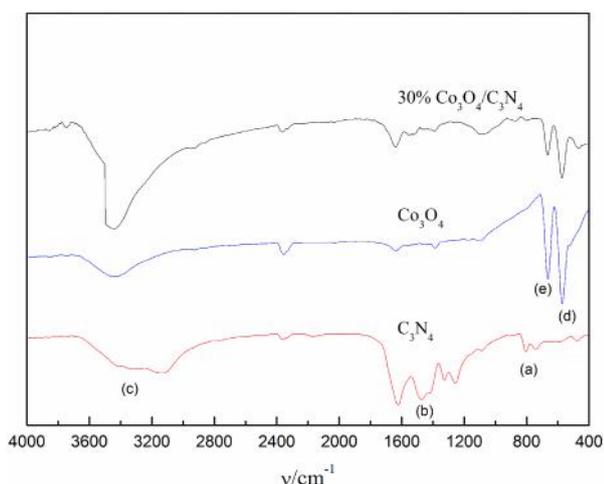


Fig.1 IR spectra of pure C₃N₄, pure Co₃O₄ and 30% Co₃O₄/C₃N₄ catalysts.

The photocatalytic degradation of methyl blue by pure C₃N₄, pure Co₃O₄ and different mass rates of Co₃O₄/C₃N₄ catalysts were studied and compared. As shown in Figure 2, the 30% Co₃O₄/C₃N₄ catalyst has the best degradation performance, which is better than those of pure Co₃O₄ and pure C₃N₄. While the other three composite catalysts has lower degradation performance. It may be explained that

their adsorption capacity of methyl blue is weaker than pure Co₃O₄ and pure C₃N₄. Due to 30% Co₃O₄/C₃N₄ showing best degradation performance comparing other catalysts, we further studied its degradation performance with different mass amount from 1.0 mg to 25.0 mg which was shown in Figure 3. It can be clearly seen that the degradation rate gradually increased to 98.4% from 66% as the dosage increase. When the dosage of catalyst increased to 25 mg, the degradation rate is only slightly increased, reaching 99.3%. This means that the amount of catalyst is also a major factor affecting the catalytic performance. However, if the mass amount of catalyst reached a certain value, the catalytic rate would not increase significantly. When the catalyst dosage of 15 mg, the catalytic effect is basically not changed, and then increase the amount of catalyst is not much significance.

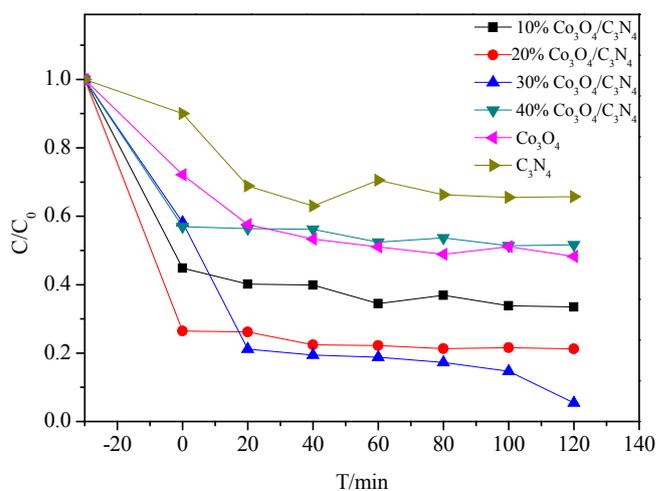


Fig.2 Photocatalytic degradation of methyl blue over pure C₃N₄, pure Co₃O₄ and different Co₃O₄/C₃N₄ composites.

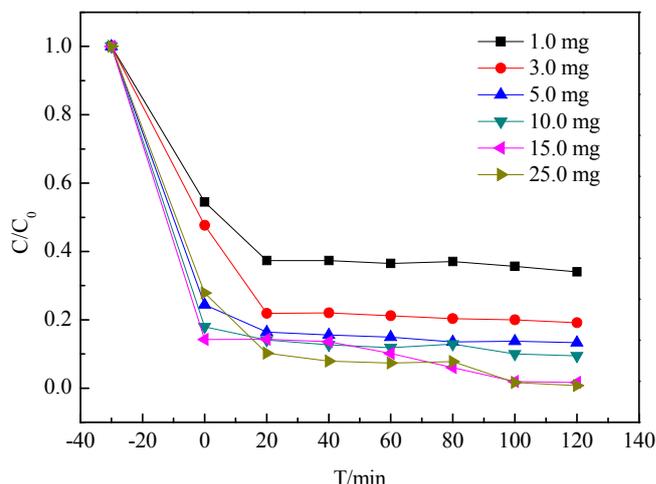


Fig.3 Photocatalytic degradation of methyl blue by 30% Co₃O₄/C₃N₄ with different mass amount.

The reuse of 30% Co₃O₄/C₃N₄ in the photocatalytic degradation of methyl blue was investigated, which is shown in Figure 4. After 4 cycles of 30% Co₃O₄/C₃N₄ composite catalyst, its degradation rate of methyl blue in the 90 min was only slightly decreased from 86.8% to 82.8% which showed good photostability and repeatability.

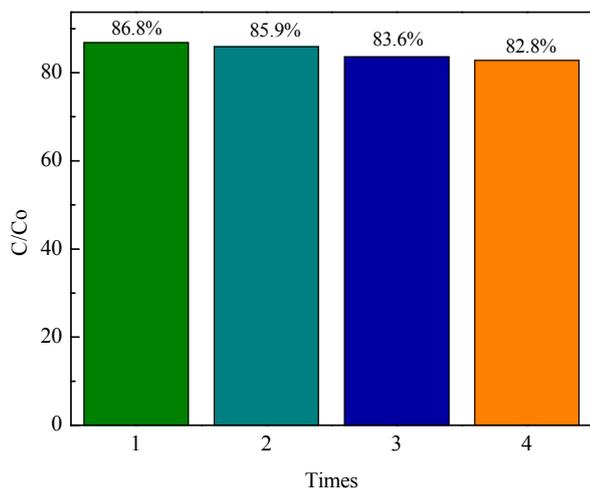


Fig.4 Recycling rate of 30% $\text{Co}_3\text{O}_4/\text{C}_3\text{N}_4$ composite catalyst.

IV. CONCLUSION

With the development of science and technology, people are facing more and more serious energy shortage and environmental pollution. As a kind of advanced oxidation technology, photocatalysis has been widely studied and applied in the field of environmental pollution control and energy development. The development of high efficiency and high stability of the photocatalyst have become a hot research on the photocatalytic science. In this paper, photocatalysts $\text{Co}_3\text{O}_4/\text{C}_3\text{N}_4$ were prepared and characterized by FT-IR spectroscopy. It can be clearly seen that the IR spectrum 30% $\text{Co}_3\text{O}_4/\text{C}_3\text{N}_4$ possess the characteristic peaks of Co_3O_4 and C_3N_4 . The photocatalytic results show that the introduction of Co_3O_4 significantly improves the optical absorption properties of C_3N_4 , which is beneficial to the separation of photogenerated electrons and holes on the surface. The prepared $\text{Co}_3\text{O}_4/\text{C}_3\text{N}_4$ for visible photocatalytic degradation of methyl blue has higher catalytic efficiency than those of pure C_3N_4 and pure Co_3O_4 . The best cobalt loading rate was 30% when the concentration of methylene blue was 40 mg/L. The reuse study of 30% $\text{Co}_3\text{O}_4/\text{C}_3\text{N}_4$ shows good photostability and repeatability after four cycles.

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