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Synthesis of Fe (OH) $_3$/g-C_3N_4 catalyst by a simple two-step method and application in organic pollutants degradation

Xiaoming Peng, Wendong Luo*

School of Civil Engineering and Architecture, East China Jiaotong University, Nanchang, Jiangxi Province, China

*Corresponding author e-mail: luowendong1216@163.com

Abstract. The photo catalyst Fe $(OH)_3$/g-C_3N_4 was successfully prepared by a simple method. Degradation performance of BP-5R by Fe$(OH)_3$/g-C_3N_4 and g-C_3N_4 was compared, the results showed that the removal rate of BP-5R by Fe$(OH)_3$/g-C_3N_4 can reached 93.9% at 1.0h, which was 2.87 times higher than that of the pure g-C_3N_4. The prepared samples were characterized and analyzed using a series of characterization methods. It was found that the enhancement of photocatalytic performance was mainly due to the transfer of photoelectrons to the Fe $(OH)_3$. At the same time, the main active species in the process of photocatalytic degradation were analyzed. The results demonstrated that the active species including h^+ and $\bullet O_2^-$ are predominant role in the photocatalytic reaction.

1. Introduction

In recent years, more and more industrial synthetic organic compounds have been widely used in the world. However, excessive use has led to a wide variety of organic pollutants entering natural water bodies, and caused incalculable harm to the ecological environment and human health. Among many organic pollutants, industrial synthetic dyes occupy a certain position. They are widely used in textile industry, leather industry and printing industry. The produced wastewater contains a large amount of organic pollutants, which can remain in the environment and difficult to completely degrade in a short time. Commonly used methods for treating wastewater include coagulation sedimentation method, adsorption method [1], biological method [2] and photocatalytic degradation method [3]. Among these methods, photocatalytic degradation method has the advantages of high degradation efficiency and without secondary pollution. At the same time, photo catalyst has excellent regenerability and can convert solar energy into chemical energy [4]. Which can solve the environment problem, at the same times can effectively deal with the current situation of energy shortage.

The low activity and high preparation cost of the catalyst limit the wide application of photo catalyst in practical engineering. Therefore, it is particularly important to develop a catalyst with low cost and high catalytic activity to solve the existing environmental and energy problems. Graphite carbon nitride (g-C_3N_4) is a potential new catalyst that can effectively solve environmental and energy problems, due to its advantages of visible light response, simple preparation method, low price of raw materials and controllable electronic properties [5]. But the drawback of g-C_3N_4 is rapid recombination of photo-induced electron-hole pairs during photo catalysis [6].

In previous studies, researchers have tried different methods to modify the material itself to enhance its photocatalytic performance. In the paper, graphite carbon nitride was prepared by thermal polycondensation method, and then the as-prepared carrier was fully mixed with ferric chloride, $Fe(OH)_3$ was uniformly loaded on the surface of g-C_3N_4 by a precipitation method, and the composite $Fe(OH)_3$/g-C_3N_4 was successfully prepared.

2. Experimental

2.1. Preparation of catalysts

Firstly, 20g of melamine was placed in a muffle furnace for heat treatment at 550℃ for 3.0 h, the obtained solid was ground to powder to obtain g-C3N4. Secondly, 5 g g-C3N4 and 125mL of FeCl3 solution (0.1mol/L) were fully mixed for 2 h, then 125mL of NaOH solution (0.2mol/L) was added, and the mixture was fully stirred at room temperature for 4 h until the mixture was completely precipitated. After filtrated, washed and dried at 105 ℃ for 24 hours, and the prepared material was designated as Fe $(OH)_3$/g-C_3N_4.

3. Results and discussion

3.1. Characterization of catalyst microstructure and chemical properties

Figs. 1(a) and 1 (b) are SEM images of as-prepared catalysts. From Fig. 1(a), a lamellar structure can be observed, and the surface of the material is very smooth, which is a typical g-C_3N_4 structure. After Fe $(OH)_3$ was loaded on its surface, obvious small blocky particles can be observed on the surface (Fig. 1(b)), the introduction of $Fe(OH)_3$ can significantly increase the specific surface area of the catalyst.

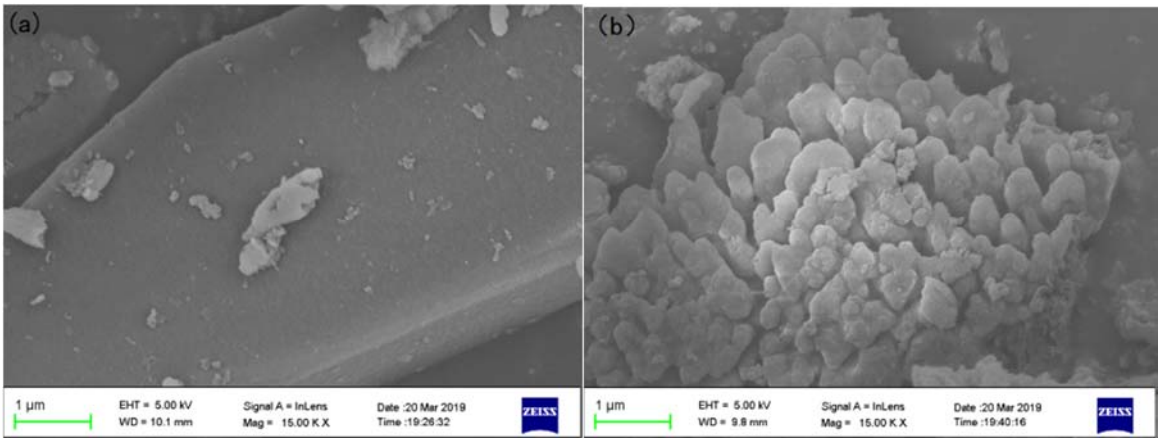

Figure 1. SEM images of g-C_3N_4 (a) and Fe $(OH)_3$/g-C_3N_4 (b)

XRD pattern of g-C_3N_4 and Fe $(OH)_3$/g-C_3N_4 are shown in Fig. 2. From the pattern, it can be observed that the two materials have common characteristic peaks at 2θ=12.8 and 27.6, which are mainly attributed to the structure of carbon nitride, the two peaks correspond to the (100) and (002) crystal planes of g-C_3N_4. The (100) crystal plane is associated with an in-plane structure packing motive, and the intense diffraction peak located at 27.5°, which is corresponds to the aromatic ring structure in g-C_3N_4, indicating that the crystal structure of g-C_3N_4 has not changed after modification. Compared with g-C_3N_4, new characteristic peaks appeared at 2θ=35.6, 41.9, 51.2 and 63.8° in the XRD pattern of Fe $(OH)_3$/g-C_3N_4 (JCPDS Card 22-0346). Suggesting the Fe $(OH)_3$ particles was successfully loaded on the surface [7].

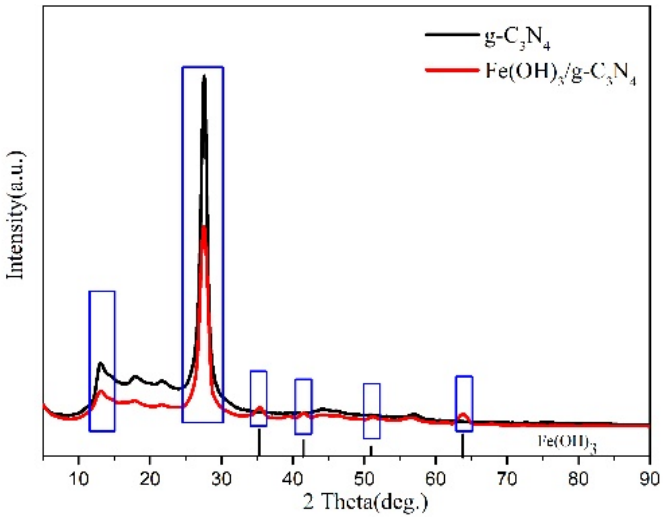

Figure 2. XRD pattern of as-prepared photo catalyst

3.2. Study on Photocatalytic Performance and Mechanism Analysis

The catalytic performance of different photo catalysts was compared by degradation of BP-5R. The reaction was carried out in a solution with BP-5R concentration of 10mg/L, and the dosage of photo catalyst was 20mg. Before the photocatalytic reaction was carried out, it was first stirred in the dark for 0.5h [8]. Photocatalytic reaction was carry out in 500W Xe lamp, and samples are taken every 10min to obtain the residual concentration of BP-5R in the solution, and the obtained data are fitted with quasi-first-order kinetic model.

From Fig. 3(a), it can be observed that the concentration of dye in the solution hardly changes after the reaction in the dark for 0.5h, which indicates that the prepared material has poor adsorption capacity. When the reaction is transferred to visible light, the concentration of dye in the solution can be quickly reduced. After 1.0h photocatalytic reaction, the removal rates of g-C_3N_4 and Fe $(OH)_3$/g-C_3N_4 to BP-5R can reach 32.7% and 93.9%, respectively. Which is 2.87 times higher than that of g-C_3N_4, after modified the photocatalytic performance is significantly improved [9]. Fig. 3(b) is the result of fitting the data in the photocatalytic reaction process with the kinetic model. From the picture, it can be observed that the fitting degrees of the two materials are 0.996 and 0.943, respectively, and the calculated rate constants are 0.00636 and 0.4346, respectively.

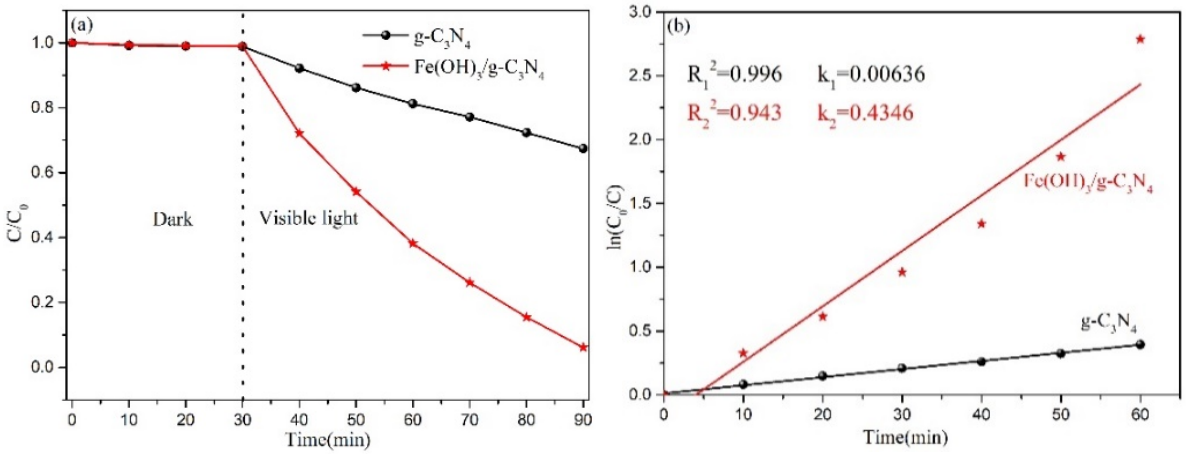

Figure 3. (a) Performance comparison of preparing photo catalyst for degradation BP-5R, (b) fitting results of photocatalytic reaction process with quasi-first-order kinetic model

Fig. 4(a) is the PL spectrum of the as-prepared photo catalyst, which measured with the excitation wavelength of 375nm. From the spectrum, it can be observed that the maximum fluorescence emission peak of g-C_3N_4 exists at about 450nm, which corresponds to the band gap where photogenerated e^--h^+ combine. The diffraction peak of $Fe(OH)_3$/g-C_3N_4 is red shift to about 462nm, and the diffraction peak intensity of the composite decreased, indicating that the modification of the material can reduce the recombination of e^--h^+ [10]. In order to study the main active species in the photocatalytic degradation of BP-5R by Fe $(OH)_3$/g-C_3N_4, sodium oxalate, p-benzoquinone (BQ) and isopropyl alcohol (IPA) are used as scavengers. The experimental results are shown in Fig. 4(b). It can be observed from the picture that Fe $(OH)_3$/g-C_3N_4 has a removal rate of 93.9% for BP-5R at 60min when without scavenger added. When sodium oxalate was added, the removal rate was 68.9%. When IPA was added, the degradation rate was basically unaffected. When BQ was added, the removal rate was only 21.5%.

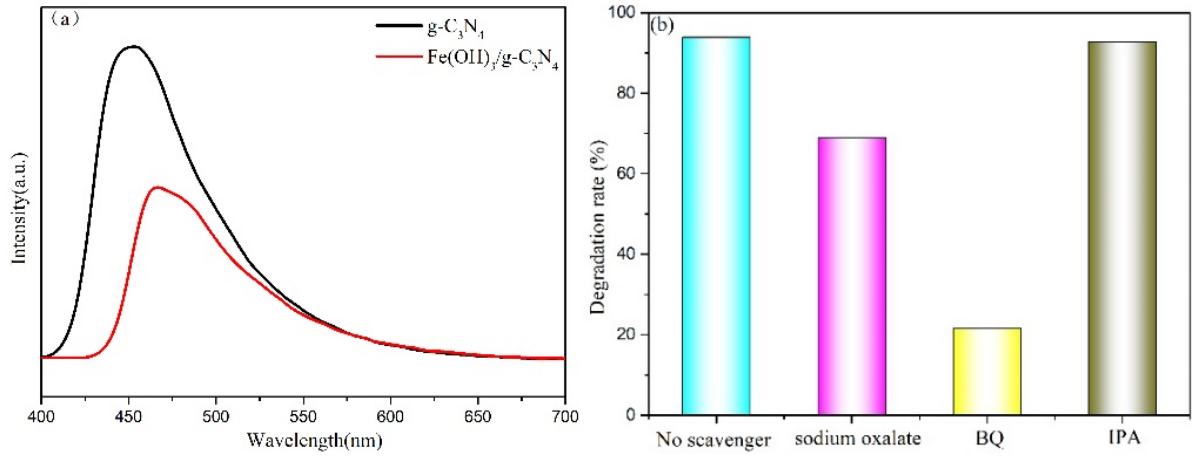

Figure 4. (a) PL spectrum of the catalyst, (b) influence of scavengers on photocatalytic degradation by Fe $(OH)_3$/g-C_3N_4

Therefore, it can be considered that the main active species in the degradation process are h^+ and $\bullet O_2^-$, and the possible degradation mechanism of BP-5R was proposed. Under the irradiation of visible light, photo-generated electrons generated by the photo catalyst transition from the VB to the CB, and a part of photo-generated electrons can combine with O_2 to generate $\bullet O_2^-$, which can reactor with BP-5R. The photo-generated electrons on the conduction band will transfer to Fe $(OH)_3$, which can more effectively inhibit the recombination of e^--h^+, which is the main factor for enhancing the photocatalytic performance of the composite material. Combined with the two active species can rapidly remove BP-5R in solution.

4. Conclusion

Graphite carbon nitride was successfully prepared by thermal polycondensation method, and then Fe $(OH)_3$ was successfully loaded on g-C_3N_4 by precipitation method. The removal rate of the prepared Fe $(OH)_3$/g-C_3N_4 to BP-5R was 2.87 times than that of g-C_3N_4. The enhancement of photocatalytic activity is attributed to $Fe(OH)_3$ loaded can effectively inhibit the recombination of e^--h^+ and increase the active species in the photocatalytic reaction process. Experiments show that the active species including h^+ and $\bullet O_2^-$ play a major role in the photocatalytic reaction process. This study provides a theoretical basis for the wide application of g-C_3N_4.

Acknowledgments

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