Performance study of erbium-doped modified graphite-phase carbon nitride catalyzed degradation of RhB

Jiashuo Chen [#,1,*], Ziyang Zhang[#,2], Nuo Chen[#,3]

[1]College of Science, Heilongjiang Bayi Agricultural University, Daqing, 163319, China

[2]School of Materials Science and Engineering, Shenyang Jianzhu University, Shenyang, 110168, China

[3]School of Materials Science and Engineering, Xiangtan University, Xiangtan, 411105, China

*Corresponding author: cjs09_11@163.com

[#]These authors contributed equally.

Abstract. In order to improve the photocatalytic ability of graphite-phase carbon nitride, Er was selected as a precursor to modify graphite-phase carbon nitride, and the graphite-phase carbon nitride composite (Er/g-C_3N_4) doped with rare earth (Er) was prepared by thermal polymerization. The results showed that the 0.5% Er/ g-C_3N_4 composite had strong visible light absorption. The results showed that the 0.5% Er/ g-C_3N_4 catalyst had a good visible light absorption and the 0.5% Er/ g-C_3N_4 catalyst had a better degradation effect on RhB.

Keywords: Graphitic-phase carbon nitride; Photocatalysis; Erbium; RhB;

1. Introduction

With the rapid development of industry and technology in recent years, people's demand for living standards is increasing, which leads to the increasing global demand for energy. At the same time, many new refractory pollutants are produced and difficult to remove. Therefore, energy shortage and environmental pollution have become major challenges to global development. Rhodamine B is a synthetic Bright peach red dye, which is often used in industrial dyeing, which is easy to cause serious water pollution and great harm to the human body [1]. In 2017, the World Health Organization listed it on the list of three categories of carcinogens. In order to purify the polluted water, there is an urgent need for an energy-saving and environmental protection method to reduce the content of rhodamine B in industrial wastewater.

The most common solutions to dye pollution are adsorption, photocatalytic degradation, coagulation-flocculation and microbial treatment [2], in which photocatalytic degradation means that after the semiconductor is excited by visible light, the electrons in the valence band will be excited to jump to the conduction band to form photogenerated electrons, and a photogenerated hole will be left in the valence band. The pollutants attached to the surface of the material are degraded into harmless small organic molecules or other inorganic substances by the action of electrons and holes. This process uses light energy to stimulate semiconductor materials to produce chemical energy, which has the advantages of low energy consumption, simple operation, easy maintenance, no secondary pollution and so on [3]. In recent years, with the introduction of the concept of metal-free catalysis[3], the research of many carbon-containing compounds in photocatalysis has attracted more and more attention[4].Among many semiconductors, graphite-phase carbon nitride (g-C_3N_4) has attracted much attention because of its special structure. It is a planar two-dimensional lamellar network structure similar to graphene, which is formed by infinite extension of triazine ring (C_3N_3) and 3murs-triazine ring (C_3N_3). The two-dimensional lamellar network is bonded by van der Waals force [5]. Graphite-phase carbon nitride (g-C_3N_4) is a narrow band gap semiconductor (2.7eV), which has a suitable band position (conduction band site -1.3eV, valence band site 1.4eV), so light absorption can be carried out around 420nm. At present, the main methods for preparing graphite carbon nitride (g-C_3N_4) phase are high temperature thermal Polycondensation, solvothermal method and electrochemical deposition method [5], in which high temperature thermal polymerization selects

one or more precursors and high temperature induces Polycondensation of precursor compounds. Generally, urea, thiourea, monocyanamide, dicyandiamide and melamine are used as precursors, and the photocatalytic activity of graphite carbon nitride (g-C_3N_4) prepared by different precursors is different. Based on the above theory, we consider the comparative analysis of the modification of graphite carbon nitride (g-C_3N_4) in order to get the best ratio of photocatalytic activity [6].

Due to the defects of graphite-phase carbon nitride (g-C_3N_4), such as fast recombination of photogenerated electron-hole pairs and poor electron transport ability, its catalytic effect will be obviously limited [7]. In order to solve these problems, scientists have proposed a number of strategies to improve the function of graphite-phase carbon nitride (g-C_3N_4), including doping non-metallic and metallic elements [8-10]. Rare earth ions have special optical properties, which can emit fluorescence for a long time, and the emission spectrum covers ultraviolet, visible and infrared bands[11]. Graphite-phase carbon nitride (g-C_3N_4) doped with rare earth ions can produce donor energy levels above the valence band (vb) to produce photogenerated electrons or acceptor levels below the conduction band to receive photogenerated electrons, which narrows the band gap of graphite-phase carbon nitride (g-C_3N_4) and increases the light absorption range, thus improving the photocatalytic efficiency of graphite-phase carbon nitride (g-C_3N_4) [12].

Therefore, in this paper, different amounts of rare earth doping in graphite-phase carbon nitride (g-C_3N_4) were compared to analyze the effect of rare earth doping on the photocatalysis of graphite-phase carbon nitride (g-C_3N_4).

2. Experiment

2.1. Sample preparation

2.1.1. Preparation of graphitic-phase carbon nitride

Weigh 15 g of thiourea in a 50 ml crucible, keep heating at 5°C/min in a muffle furnace, wait until the temperature of the muffle furnace reaches 550°C, keep constant temperature for 4h, cool naturally to room temperature, remove the product for crushing and grinding, obtain a light yellow solid which is graphite-phase carbon nitride (g-C_3N_4).

2.1.2. Preparation of erbium-doped modified graphite-phase carbon nitride

Weigh 15 g of thiourea into a 50 ml crucible, weigh a series of gradient molar mass percentages (molar mass of erbium as a percentage of molar mass of urea) of erbium and urea for homogeneous mixing, the series of gradient molar mass ratios are: 0.1%-0.9%; the sample is placed in a muffle furnace, and the temperature is continuously increased at 5°C/min, and when the temperature of the muffle furnace reaches 550°C, the constant temperature is maintained for 4h, and naturally cooled The product was taken out and crushed and ground, and the solid was obtained as Erbium-doped modified graphitic phase carbon nitride (Er/g-C_3N_4).

2.2. Photocatalytic experiments

2.1.3. Photodegradation catalysis experimental procedure

A xenon lamp was used as the light source to disperse 0.1g of sample powder in 100ml of RhB aqueous solution at a mass concentration of 10mg/L. The sample was placed in a dark environment at a controlled temperature of 25℃ and stirred for 2h to achieve adsorption-desorption equilibrium of RhB molecules in the dispersion.

2.1.4. Indicators for the assessment of photodegradation catalysis experiments

（1）Dynamical models

The catalyst activity was assessed using the rate of degradation of rhodamine by the catalyst ln(C_0/Ct) and the primary kinetic constant, the reaction rate constant was calculated by a quasi primary kinetic model with the following equation.

$$\ln\left(\frac{C_0}{C_t}\right) = k \times t \quad (1)$$

C_t ： the concentration corresponding to RhB at moment, mg/L;

C_0 ： the solubility corresponding to RhB at the initial moment, mg/L;

k: the quasi primary kinetic constant, min^{-1};

t: time, min;

（2）Degradation rate model

The concentration of RhB was chosen as an indicator to establish an equilibrium relationship between concentration and absorbance to model the degradation rate：

$$\beta = \frac{C_0 - C_t}{C_0} \times 100\% = \frac{A_0 - A_t}{A_0} \times 100\% \quad (2)$$

β: the degradation rate of RhB;

C_t : the concentration corresponding to RhB at moment t, mg/L;

C_0: the solubility corresponding to RhB at the initial moment, mg/L;

A_t: the absorbance corresponding to RhB at moment；

A_0: the absorbance corresponding to RhB at the initial moment.

3. Analysis of results

3.1. FT-IR analysis

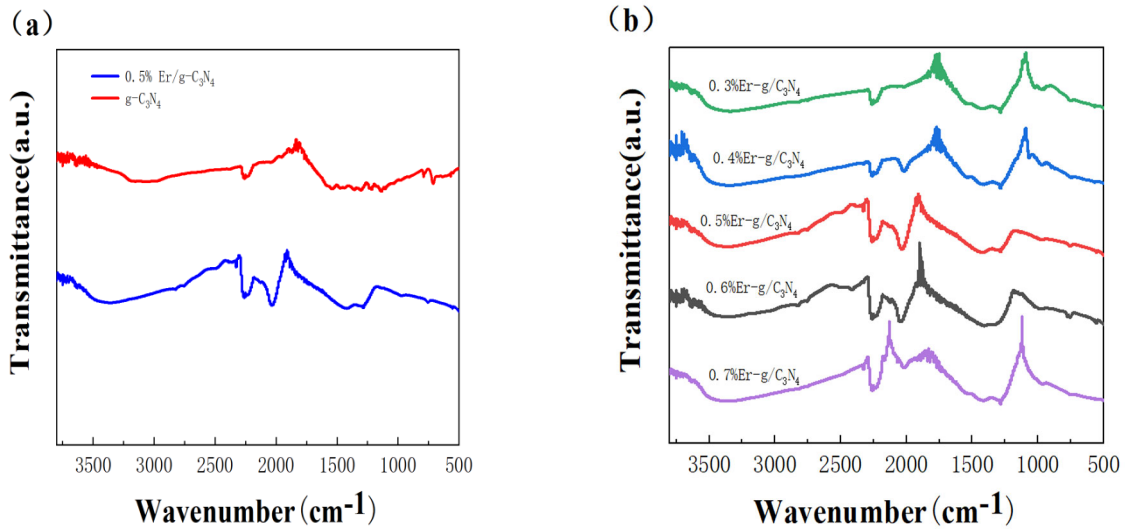


Fig.1 Different doping amounts of FI-IR analysis

For the infrared spectrum of g-C_3N_4, the absorption peaks of the N-H bond stretching vibration of g-C_3N_4 are significantly wider in the range of 3082-3372 cm^{-1}, the characteristic absorption peaks of the aromatic carbon-nitrogen heterocyclic unit of g-C_3N_4 are in the range of 1242-1727 cm^{-1}, showing multiple and more intense peaks, and the characteristic absorption peaks of the 3-s triazine structure of g-C_3N_4 are at 782 cm^{-1}. The characteristic absorption peak of the 3-s triazine structure of g-C3N4 is found at 782 cm^{-1} [13,14]. By FI-IR analysis, it is obvious from Figure 1(a) that the erbium-doped modified graphite-phase carbon nitride is similar to the graphite-phase carbon nitride in terms of characteristic peaks. Figure 1(b) shows the FT-IR spectra of the modifications with different levels of Er doping (0.3%, 0.4%, 0.5%, 0.6%, 0.7%), the centre of the band between 2290 and 2390 cm^{-1}

belongs to the C-N stretching vibration, indicating the formation of C≡N triple bonds rather than the typical aromatic C-N stretching vibration [15]. Er doping breaks some of the triazine rings of g-C3N4, transforming the sp^2 C-N single bond into a C≡N triple bond, with its 0.5% Er/ g-C_3N_4 having a larger peak in this band, demonstrating the better effect of Er doping compared to other doping contents.

3.2. Photocatalytic degradation analysis

3.2.1 Comparison of the performance of a range of gradient doping materials

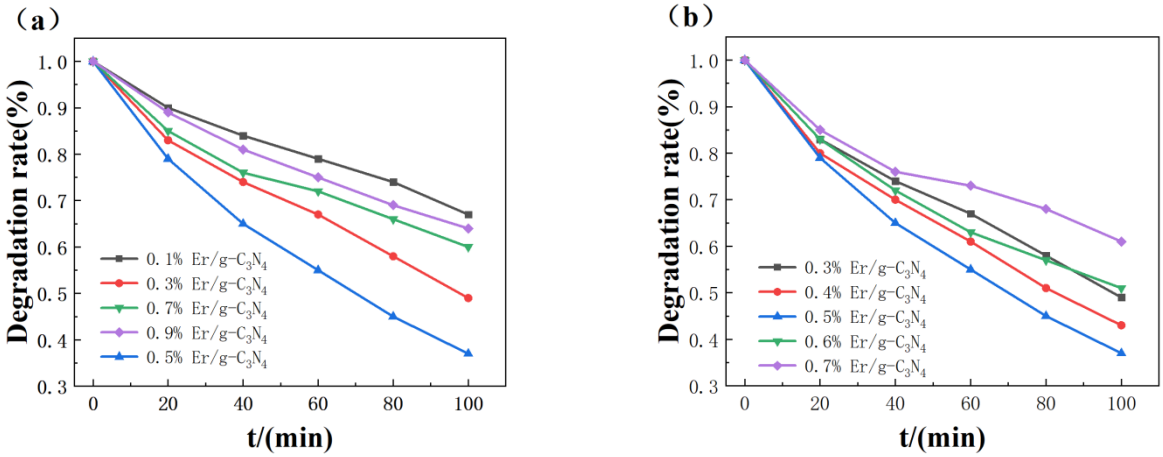


Fig.2 Degradation of RhB by different erbium doping levels

Judging by the degradation rate model, it can be seen from the above figure: under the same light conditions, a series of gradient doping amounts were set, as shown in Figure 2（a）, within the gradient of 0.1%-0.9%, the degradation efficiency of 0.5% erbium doping amount for rhodamine B was significantly higher than other doping amounts. Meanwhile, the gradient ratio was scaled down and adjusted to 0.3%-0.7% erbium doping, as shown in Figure 2(b), and it was further found that 0.5% erbium doping was more effective in degradation.

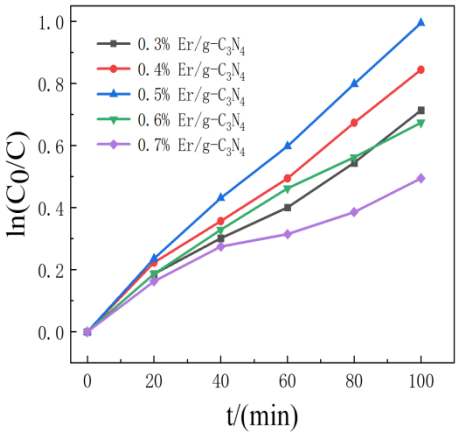


Fig.3 Kinetics of RhB degradation by different erbium doping levels

Further judged by the kinetic model, as can be seen from Figure 3 above: different kinetic constants were calculated for 0.3%-0.7% erbium doping under the same light conditions, and the kinetic constants are shown in Table 1 below, and it was further found that the kinetic constants were larger for 0.5% erbium doping, corresponding to its better degradation effect.

Table 1 Kinetic constants for the degradation of RhB by different erbium doping levels

Doping amount	0.3%	0.4%	0.5%	0.6%	0.7%
k/(min^{-1})	0.71335	0.84397	0.99425	0.67335	0.49300

3.2.2 Comparison of the performance of better doped materials

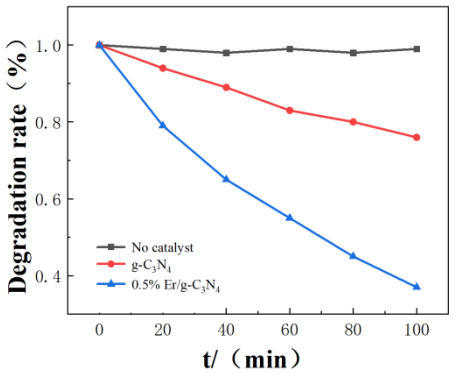


Fig.4 Efficiency curves for photocatalytic degradation of RhB

The better doped material was selected for performance comparison with graphitic phase carbon nitride, and the system without the addition of photocatalyst had a weak and negligible effect on RhB degradation for a given time under the same light conditions. As shown in Figure 4: the degradation of RhB for the systems with the addition of g-C3N4, 0.5% Er/ g-C3N4 for the same time and under the same conditions were: 24%, 63% respectively.

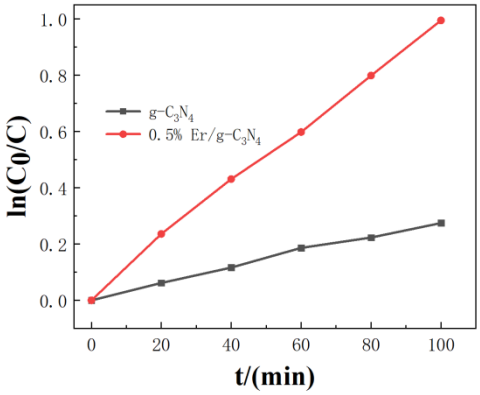


Fig.5 Kinetic constant diagram for the photocatalytic degradation of RhB

Table 2 Kinetic constants for photocatalytic degradation of RhB

Category	$g\text{-}C_3N_4$	$0.5\%Er/g\text{-}C_3N_4$
$k/(min^{-1})$	0.274437	0.994252

The catalytic degradation of RhB by different photocatalyst systems was evaluated using the primary kinetic constants in Table 2 below, which were 0.274437, 0.994252, and 0.5% Er/ g-C3N4 to enhance the absorption of visible light to achieve high degradation performance of RhB as shown in Figure 5.

4. Conclusions

The characterization of $Er/g\text{-}C_3N_4$ nanomaterials and their degradation efficiency of RhB revealed that the modification of $g\text{-}C_3N_4$ with Er improved the visible light absorption of $g\text{-}C_3N_4$ nanomaterials and effectively inhibited the compounding of photogenerated electrons and holes, resulting in a lower carrier compounding rate and ensuring sufficient photogenerated electrons for the photocatalytic degradation of RhB.

A series of gradient erbium doping levels were set up for comparison, and a model analysis of the degradation efficiency of RhB showed that its 0.5% erbium doping level was a better doping level. Under the same experimental conditions, its degradation efficiency of RhB was significantly higher than that of other doping amounts.

Analysis of the degradation process of RhB by kinetic modelling showed that compared to its degradation of g-C_3N_4 with a kinetic constant of 0.274437, 0.5% Er/g-C_3N_4 increased its kinetic constant to 0.994252.

The catalytic efficiency of 0.5% Er/g-C_3N_4 compared to g-C_3N_4 for the photocatalytic degradation of rhodamine B and its kinetic constants were found to be significantly higher due to the modification of g-C_3N_4 by the rare earth element Er and under the same comparative conditions.

References

[1] Nandigana Pardhasaradhi, Mahato Sanchayan, Dhandapani Manjubashini, et al. Lyophilized tin-doped MoS2 as an efficient photocatalyst for overall degradation of Rhodamine B dye [J]. Journal of Alloys and Compounds Volume 907, 25 June 2022, 164470.

[2] Chen Zhangxu, Fu Minglian, Zhu Danchen, Zheng Bingyun.Preparation and removal of methylene blue from carbon/graphite carbon nitride composites[J/OL].Inorganic Salt Industry:1-10[2022-08-30].DOI:10.19964/j. issn.1006-4990.2022-0283.

[3] Deb Mohit L, Saikia B Shriya, Rahman Iftakur, et al. Metal-Free Catalysis in C-C Single-Bond Cleavage: Achievements and Prospects [J]. Metal-Free Catalysis in C-C Single-Bond Cleavage: Achievements and Prospects.

[4] Hu Fupeng, Zhou Yueling, Duan limin, Jia Chenghao, she Zhixiang, Wang Jin. effect of pH value on visible light catalytic degradation of rhodamine B by g-C3N4 [J]. Journal of Hefei University of Technology (Natural Science Edition), 2021, 44 (11): 1545-1550.

[5] Praus, Petr A brief review of s-triazine graphitic carbon nitride [J]. Carbon Letters2022. PP 1-10

[6] Liu Xiang, Tian Jian. Gold nanorods / g-C3N4 heterostructures are used for photocatalytic hydrogen production under visible and near infrared light [C] / /. Proceedings of the 7th Symposium on Science and Technology of New Solar Cell Materials. [publisher unknown], 2020: 425.DOI: 10.26914/c.cnkihy.2020.006565.

[7] Mei Xueting, Chen Shujun, Wang Gangqiang, et al. Metal-free carboxyl modified g-C3N4 for enhancing photocatalytic degradation activity of organic pollutants through peroxymonosulfate activation in wastewater under solar radiation [J]. Journal of Solid State ChemistryVolume 310, 2022.

[8] Wang Xiaoshuang, Li Yuzhen, Yi Siyuan, Gao Lizhen. Bi2MoS2O4 modified g-C3N4 photocatalytic degradation of Rhodamine B[J]. Journal of Composite Materials, 2022,39(08): 3845-3851.DOI:10.13801/j .cnki.fhclxb.20210917.002.

[9] Han Jinshuai. Study on the promotion of photocatalytic activity of g-C3N4 by different modification methods [D]. Yanshan University, 2021.DOI:10.27440/d.cnki.gysdu.2021.001361.

[10] Chen Yanfang. Modification of g-C3N4 constructed by molecular doping and its photocatalytic activity [D]. Qingdao University of Science and Technology, 2022.DOI:10.27264/d.cnki.gqdhc.2022.001181.

[11] Wei Tiantian. Preparation and analytical application of doped graphite phase carbon nitride and GQDs [D]. Nanchang University, 2017.

[12] Zheng Wanle, Pan Yusong, Pan Chengling. Research progress in photocatalysis of rare earth doped graphitic carbon nitride [J]. China Ceramics, 2021, 57(09): 19-25. DOI: 10.16521/j.cnki.issn.1001 - 9642.2021.09.003.

[13] Zhang Qian. Preparation of MIL-125(Ti) and modified MIL-125(Ti) and its catalytic properties [D]. Tianjin: Tianjin University of Technology, 2017:6-60. ZHANG Qian. Preparation and catalytic properties of MIL-125(Ti) and modified MIL-125(Ti) [D]. Tianjin: Tiangong University, 2017:6-60.

[14] Long Xinxin, Feng Chuanping, Yang Shengjiong, Ding Dahu, Feng Jinpeng, Liu Meng,Chen Yang, Tan Jihua, Peng xingjie, Shi Jinan, Chen Rongzhi. Oxygen doped graphitic carbon nitride with regulatable local electron density and band structure for improved photocatalytic degradation of bisphenol A [J]. Chemical Engineering Journal,2022,435(P1).

[15] Hayat Asif, Al-Sehemi Abdullah G., El-Nasser Karam S., Taha T.A., Al-Ghamdi Ahmed A., Jawad Ali Shah Syed ,Amin Mohammed A., Ali Tariq, Bashir Tariq, Palamanit Arkom,Khan Javid, Nawawi W.I.. Graphitic carbon nitride (g–C3N4)–based semiconductor as a beneficial candidate in photocatalysis diversity [J]. International Journal of Hydrogen Energy, 2022,47(8).