

Visible Light Catalytic Degradation of Dye Wastewater using Carbon Nitride

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Abstract. Graphite phase carbon nitride (g-C₃N₄) as a novel semiconductor photocatalysts attracted widespread attention in recent years. In this paper, the lamellar g-C₃N₄ nano-materials prepared from solid urea was used as a photocatalyst to degrade the simulated dye wastewater under visible light irradiation. In addition, the photocatalytic degradation performances of g-C₃N₄ material prepared from conventional and mechanical-conventional methods for degrading organic dye solutions were compared and discussed in detail. The Rhodamine B (RhB), Methylene Blue (MB) and Methyl Orange (MO) water solutions were chosen as simulated dye wastewater. The results showed that these two kinds of C₃N₄ photocatalyst both has a high decoloration efficiency for these three dyes using visible light. Compared with that from conventional method, the g-C₃N₄ from mechanical-conventional method has a higher photocatalytic performance, which offered a new process for preparing graphite phase carbon nitride. The molecule structure of dye has an effect on the visible-light decoloration efficiency of g-C₃N₄. Also, the absorption capability of dye molecules on catalyst gave an important role during this visible-light irradiation process.

Introduction

Environment pollution and energy crisis are two of the most serious problems which are facing humanity today. The photocatalytic technology provides a brand new and promising solution for environmental issues. Therefore, it attracts worldwide attention due to it can absorb solar light to decompose the environmental pollutants. However, the practical application of traditional photocatalysts (such as TiO₂) is severely limited due to their low utilization rate of solar light and poor quantum yield^[1]. Therefore, exploration of high efficient photocatalysts with large specific surface area and high quantum yield becomes one of the important aims for semiconductor photocatalytic technology. The novel organic polymer semiconductor photocatalyst, graphite carbon nitride (g-C₃N₄), has drawn much attention for its unique properties such as visible light respond, high chemical and thermal stability, environmental compatibility and economical capability. However, the photocatalytic activity of g-C₃N₄ is low due to its small specific surface area and low quantum yield. In this paper, we mainly focus on the improvement of the photocatalytic activity of g-C₃N₄ by using mechanical treatment for enlarging its surface area.

In this paper, the prepared g-C₃N₄s using conventional method and mechanical-conventional method were used to photocatalytically degrade the organic dyes Rhodamine B (RhB), Methylene Blue (MB) and Methyl Orange (MO) under visible light conditions. The degradation performance of the prepared g-C₃N₄ for the dye solutions was compared and discussed detailly.

Experimental

Materials. Urea (analytical grade, solid powder, 99.5 %) was purchased from Sigma Chemicals Company. Rhodamine B, Methyl orange and Methylene Blue were supplied by Jinan Dye Company. All the chemicals were used without purification.

Methods.

Preparation of g-C₃N₄ Catalyst

The g-C₃N₄ was prepared in this paper using two different methods. One is conventional method. The other one is mechanical-conventional method. For the conventional method, the urea powder was directly put into a ceramic crucible firstly, and then the crucible was placed into a muffle furnace and heated to 400 °C, and then calcined at this temperature for 1 h. After that, the sample was cooled to room temperature by itself in muffle furnace. When the temperature was decreased to room temperature, the ceramic crucible containing sample in the muffle furnace was again heated and make its temperature increase to 450 °C uniformly, and held at 450 °C for 2 hours. Throught this calcination, the powder in ceramic crucible was considered as the conventional g-C₃N₄. The preparation of mechanical-conventional g-C₃N₄ using the same procedure as that of conventional g-C₃N₄ preparation. The only difference is that the urea was firstly grinded to pass the 500 mesh screen and then put the grinded powder in the ceramic crucible to follow the procedure which was used for preparing conventional g-C₃N₄.

X-ray diffraction (XRD) analysis

The D8-ADVANCE XRD analyzer was used to record the spectrum of carbon nitride prepared in this paper. The test conditions were $\lambda=1.5442\text{nm}$, 40 mA, 40 KV, scan speed 1.8°min^{-1} , scan range $2\theta=5\sim90^\circ$.

Photocatalytic degradation of simulated dye wastewater

Weighed amount of catalyst was put into the simulated dye wastewater solution (dye concentration, 5 mg/L) firstly and then the solution was mixed at 200 rpm for 1 min using stirrer. After that, the beaker containing the dye solution and carbon nitride catalyst was put in a dark place and ultrasounded 30 min. The ultrasounded solution was then put into the photocatalytic reactor which equipped with visible light source which gives light with wavelength higer than 420 nm. After certain time of reaction, part of the dye solution was taken out of the beaker and centrifugated 10 min at 12000 rpm. The supernatant was used to measure the dye concentration in the solution based on the absorbance value at the characteristic wavelength of each dye using UV-visible spectrophometer (8435 UV-Visible Spectrophotometer from Agilent Technologies) and calculate the decoloration ratio using the following equation.

$$\text{decoloration ratio, \%} = \left(1 - \frac{C}{C_0}\right) \times 100$$

C-dye concentration after photocatalytic degradation, mg/L; C₀- initial dye concentration, mg/L

Results and discussion

XRD analysis. The XRD spectra of conventional C₃N₄ and mechanical-conventional C₃N₄ were recorded using D8-ADVANCE XRD analyzer and the spectrum of mechanical-conventional C₃N₄ was presented in Figure 1. The spectrum of conventional C₃N₄ has the similar characteristic peak as that of mechanical-conventional C₃N₄. Figure 1 showed that there was two characteristic peaks in the spectrum, at 27.5° and 13.1° respectively. In addition, a wide adsorbance peak appeared in the range of 25~30°, which corresponded to the 002 crystal plane of carbon^[2]. According to the Bragg equation, the interlamellar spacing is 0.33 nm, illustrating that the sample has graphite-type structure. The peak appeared at around 13.1° corresponded to the 100 crystal plane of carbon, illustrating the sample has the structure of Tri-s-triazine (C₆N₇) structure^[3].

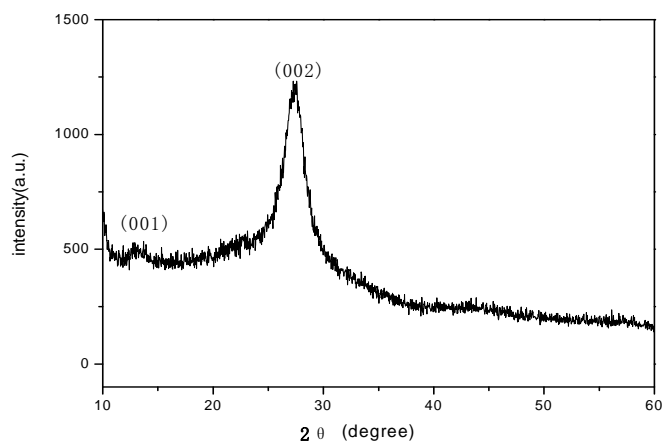


Fig.1 The XRD pattern of the sample

Photocatalytic performance of g-C₃N₄ for simulated dye solutions.

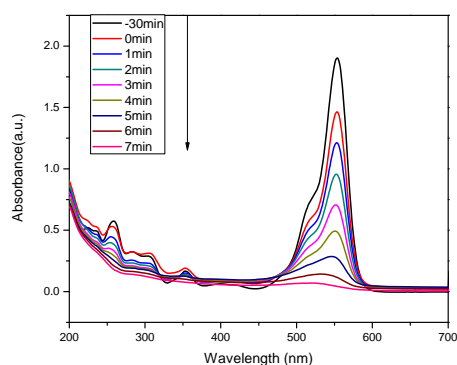


Fig.2 RhB degradation of UV-visible spectra of RhB using conventional g-C₃N₄

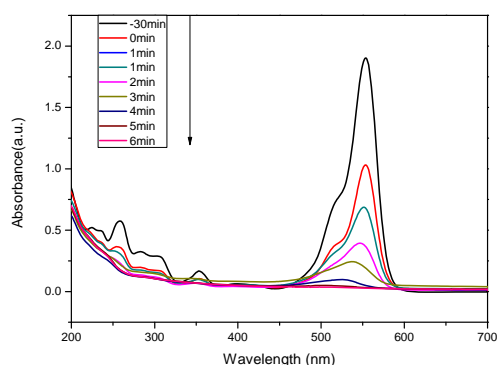


Fig.3 RhB degradation of UV-visible spectra of RhB using mechanical-conventional g-C₃N₄

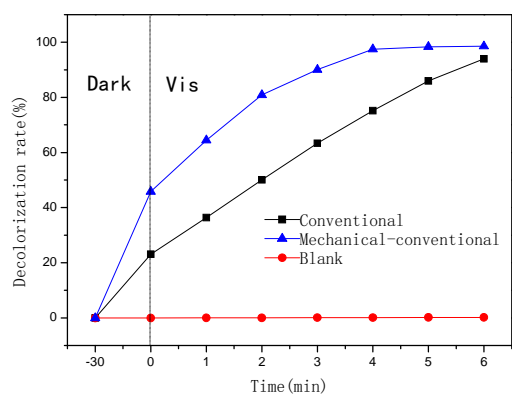


Fig.4 RhB decolorization at different time using conventional and mechanical-conventional g-C₃N₄

The UV-visible spectra of RhB dye solution during degradation using conventional g-C₃N₄ and mechanical-conventional g-C₃N₄ as photocatalytic material were presented in Figure 2 and 3. As shown in Figure 2 and Figure 3, the absorbance of characteristic peak of RhB dye solution decreased gradually with the increase of treatment time no matter the g-C₃N₄ is prepared from conventional method or mechanical-conventional method, illustrating that these two g-C₃N₄ both have the photocatalytic capability to degrade the RhB dye. For the conventional g-C₃N₄, the decoloration ratio reached 97.8 % when the treatment time reached 7 min. However, the decoloration ratio reached 98.3 % at treatment time 5 min when using mechanical-conventional

$g\text{-C}_3\text{N}_4$, which is higher than that of conventional $g\text{-C}_3\text{N}_4$. As shown, through simulation of visible light catalytic degradation, the intensity of the absorption peak of RhB dye solution gradually becomes smaller, while the pink color of the dye solution gradually faded. According to the literatures, this process is a gradual removal of the ethyl groups and the opening of ring structure in the RhB molecules [4].

Figures 4 presented the decoloration ratio of RhB dye solution during photocatalytic degradation. As shown in Figure 4, during the dark ultrasonic treatment, before the photocatalytic reaction, the decoloration ratio of mechanical-conventional $g\text{-C}_3\text{N}_4$, 45 %, is much higher than that of conventional $g\text{-C}_3\text{N}_4$, 23 %, which illustrated the mechanical-conventional $g\text{-C}_3\text{N}_4$ has a higher adsorption capability than the conventional $g\text{-C}_3\text{N}_4$ for RhB dye, resulted in the higher photocatalytic capability for RhB dye solution. When the photocatalytic time is 4 min, the decoloration ratio of the dye solution reached 96.5 % for using mechanical-conventional $g\text{-C}_3\text{N}_4$, however, it is only 79.5 % for using conventional $g\text{-C}_3\text{N}_4$, which is 17 % lower. Also, Figure 4 presented that the RhB dye can be easily decolorized or decomposed when using the prepared $g\text{-C}_3\text{N}_4$ as a photocatalytic material under visible light irradiation.

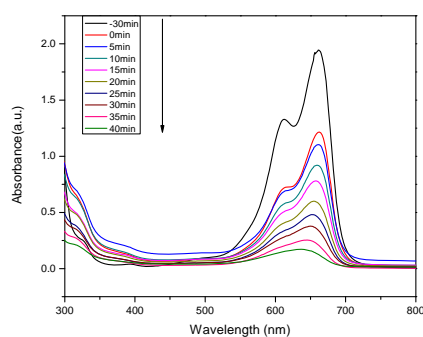


Fig.5 UV-visible spectra of MB dye solution using conventional $g\text{-C}_3\text{N}_4$

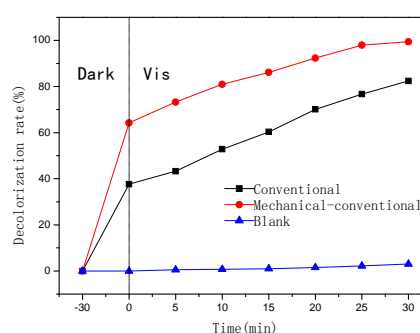


Fig.6 MB decolorization at different time using conventional and mechanical-conventional $g\text{-C}_3\text{N}_4$

Absorbance peak at characteristic wavelength decreased gradually with the prolonging of irradiation time. The decoloration ratios of MB dye solution using conventional and mechanical-conventional $g\text{-C}_3\text{N}_4$ as visible light catalyst were presented in Figure 6. Figure 6 presented that the dye concentration in the solution decreased a lot after the dark ultrasound treatment, demonstrating that the prepared $g\text{-C}_3\text{N}_4$ has a stronger absorption for MB dye than that of RhB dye. Also, the mechanical-conventional $g\text{-C}_3\text{N}_4$ has a higher absorption capability than the conventional $g\text{-C}_3\text{N}_4$, as shown in Figure 6. Compared with conventional $g\text{-C}_3\text{N}_4$, the mechanical-conventional $g\text{-C}_3\text{N}_4$ gives a higher catalytic performance for MB dye solution. When the treatment time was 30 min, the decoloration ratio reached 99 % for mechanical-conventional $g\text{-C}_3\text{N}_4$, which is much higher than that of the conventional $g\text{-C}_3\text{N}_4$, 82 %. As known, during the process of light photocatalytic degradation of organic pollutants, the catalyst can generate hydroxyl radicals ($\bullet\text{OH}$) and at the same time form electron holes (H^+) in the catalyst under the light irradiation, which can further form superoxide radical ($\bullet\text{O}_2^-$) and hydroxyl radical ($\bullet\text{OH}$) to oxidize and degrade the pollutants [5, 6, 7].

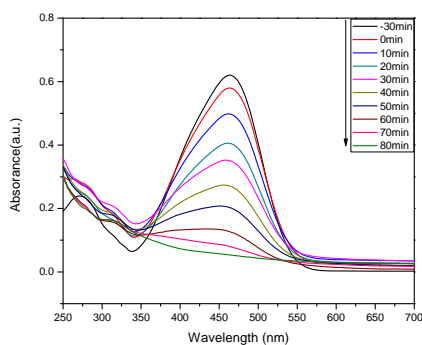


Fig.7 UV-visible spectra of MO dye solution using conventional $g\text{-C}_3\text{N}_4$

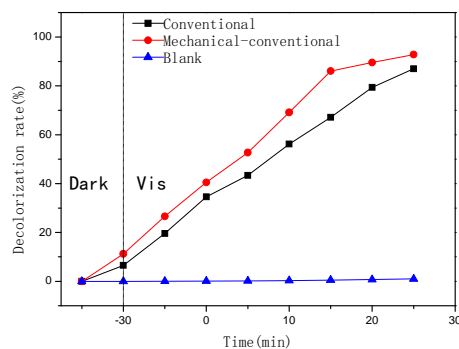


Fig.8 MO decolorization at different time using conventional and mechanical-conventional $g\text{-C}_3\text{N}_4$

The change of UV-Visible spectra of MO dye solution during photocatalytic irradiation was shown in Figure 7. It can be seen that the absorbance peak at characteristic wavelength decreased gradually with the prolonging of irradiation time. During this process, the orange color of the MO dye solution faded. The decoloration ratios of MO dye solution using conventional and mechanical-conventional $g\text{-C}_3\text{N}_4$ as visible light catalyst were presented in Figure 8. Figure 8 showed that the dye concentration in the solution decreased a bit after the dark ultrasound treatment, only around 10 % which is much lower than that of MB and RhB dye solution, demonstrating that the prepared $g\text{-C}_3\text{N}_4$ has a weak absorption for MO dye than that of MB and RhB dye. Also, the mechanical-conventional $g\text{-C}_3\text{N}_4$ has a little higher absorption capability than the conventional $g\text{-C}_3\text{N}_4$, as shown in Figure 8. Compared with conventional $g\text{-C}_3\text{N}_4$, the mechanical-conventional $g\text{-C}_3\text{N}_4$ gives a higher catalytic performance for MO dye solution. When the treatment time was 70 min, the decoloration ratio reached 93 % for mechanical-conventional $g\text{-C}_3\text{N}_4$, which is higher than that of the conventional $g\text{-C}_3\text{N}_4$, 86 %.

Compared the decoloration ratio of these three dyes (RhB, MB and MO) using conventional and mechanical-conventional $g\text{-C}_3\text{N}_4$ as visible light catalyst, it can be found that these two $g\text{-C}_3\text{N}_4$ has different decoloration efficiency based on the dye structure. Also, the absorption capability of dye molecules on catalyst gave an important role during this visible-light irradiation process.

Summary

The graphite carbon nitride, $g\text{-C}_3\text{N}_4$, was prepared successfully using solid urea through the conventional method and the mechanical-conventional method. Both the conventional $g\text{-C}_3\text{N}_4$ and mechanical-conventional $g\text{-C}_3\text{N}_4$ can be used to decolorize the dye solution. Under the visible light irradiation, the $g\text{-C}_3\text{N}_4$ s gave a good decoloration ratio. The decoloration ratio reached higher than 85 % for using conventional $g\text{-C}_3\text{N}_4$, 95 % for using mechanical-conventional $g\text{-C}_3\text{N}_4$. The molecule structure of dye has an effect on the visible-light decoloration efficiency of $g\text{-C}_3\text{N}_4$. Also, the absorption capability of dye molecules on catalyst gave an important role during this visible-light irradiation process.

Acknowledgements

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