



Processing graphitic carbon nitride for improved photocatalytic activity



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ARTICLE INFO

Available online 19 March 2014

Keywords:

Photocatalyst

g-C₃N₄

RhB

Hydrothermal process

ABSTRACT

In order to improve the photocatalytic activity of graphitic carbon nitride (g-C₃N₄), the as-prepared samples were processed by acid etching followed by thermal treatment. The specific surface area of the g-C₃N₄ increased from 11.5 to 81.5 m²/g, and many mesoporous pores were formed after hydrothermal and thermal treatment. Compared with the as-prepared g-C₃N₄, the photocatalytic activity of the treated g-C₃N₄ photocatalysts is significantly enhanced towards the degradation of RhB under visible light irradiation. The kinetic rate constant of the treated g-C₃N₄ is 6.3 times of that of the pristine g-C₃N₄. The enhancement of the photocatalytic activity of the catalysts can be ascribed to their improved specific surface area and the N-vacancy in g-C₃N₄. The N-vacancy in the structure of g-C₃N₄ decreases the bandgap of carbon nitride, thus enhances the visible light absorption. The higher specific surface area of the treated g-C₃N₄ enhances the adsorption towards RhB, and provides more active sites as well, thus higher photocatalytic activity was achieved.

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1. Introduction

Environmental issues and energy crisis are becoming rigorous test for human beings with explosive growth of population and rapid industrialization all over the world [1,2]. The photocatalytic technology provides a novel and promising solution for these issues, thus it has attracted worldwide interest due to its environmental compatibility and money-saving capability. Since Fujishima and Honda first reported the photocatalytic property of TiO₂ in 1972 [3], many efforts have been focused on developing photocatalysts based on various semiconductors in the past decades [4–16].

Recently, a metal free visible light driven photocatalyst, graphitic carbon nitride (g-C₃N₄), which is the most stable

material of all the carbon nitride allotropes under ambient conditions, has attracted intense interest for its unique properties such as thermal stability, high chemical inertness, non-toxicity, easy modification and outstanding electrical property [16–19]. g-C₃N₄ has been used as a photocatalyst for hydrogen generation and pollutant degradation. However, the photocatalytic activity of pure g-C₃N₄ towards degradation of organic pollutants is low. In order to improve the photocatalytic property of g-C₃N₄, many approaches have been developed, such as (1) using a template or acid treatment to increase its surface area [16,20–24], (2) doping heteroatoms to decrease its bandgap [25–29], and (3) coupling with other semiconductors to form heterojunction photocatalysts for depressing the recombination of electron-hole pairs [30–32]. In recent years, researchers reported that the defects in photocatalysts played an important role to affect the photocatalytic reactions. The defects in the photocatalysts can modify their electronic structure, which causes the change of the

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bandgap. In addition, defects also may act as specific reaction points for reactants [33,34].

High surface area $g\text{-C}_3\text{N}_4$ and doped $g\text{-C}_3\text{N}_4$ have been reported, which both showed improved photocatalytic activity [24,25–29]. However, there are few reports on vacancy of $g\text{-C}_3\text{N}_4$ with high specific surface area. In this study, we developed a simple method for preparing N-vacancy $g\text{-C}_3\text{N}_4$ with high surface area. The specific surface area of N-vacancy $g\text{-C}_3\text{N}_4$ is significantly increased, while its bandgap decreased. It shows excellent photocatalytic activity towards degradation of rhodamine B (RhB), compared with the as-prepared $g\text{-C}_3\text{N}_4$. This study provides a simple way to improve the surface area and decrease the bandgap of $g\text{-C}_3\text{N}_4$.

2. Experimental section

2.1. Preparation

All reagents were of analytical grade and used without further purification. Deionized water was used for the preparation of all solutions. The $g\text{-C}_3\text{N}_4$ was prepared by heating melamine at 550 °C for 2 h in a muffle. Then, the as-prepared $g\text{-C}_3\text{N}_4$ was ground to powder by agate mortar. An appropriate amount of $g\text{-C}_3\text{N}_4$ was dispersed in 40 mL HCl solution (1.0 M) under stirring for 0.5 h. After that, the mixture was transferred to a Teflon-lined autoclave (50 mL). The autoclave was sealed and heated at 150 °C for 4 h. After being cooled down to room temperature, the product was collected by filtration, and then dispersed again in 40 mL of 2.0 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ under stirring for 0.5 h. The sample was filtered and washed with distilled water and ethanol for several times, and then dried at 80 °C for 10 h. Finally, the product was annealed at 530–600 °C for 0.5–1 h in a tube furnace under N_2 atmosphere (200 mL/min). The samples were named as $\text{CN}_x\text{-y}$, x is the annealing temperature, and y denotes the annealing time.

2.2. Apparatus

Structure and phase characterization of the products was examined by X-ray diffractometer (XRD, Bruk GADDS diffractometer) with an area detector operating at a current of 40 mA using $\text{Cu K}\alpha$ radiation. The morphology of the samples was observed by scanning electron microscopy (SEM, JSM-6380-LA, JEOL, Japan). X-ray photoelectron spectroscopy (XPS) was conducted using Model VG ESCALAB apparatus with an $\text{Al K}\alpha$ X-ray source to analyze the surface composition of the samples. The Fourier transform infrared spectra (FTIR) of the products were recorded using an IR Affinity-1 FTIR spectrometer. Photoluminescence (PL) measurements were carried out on a Hitachi F-4500 fluorescence spectrophotometer. UV–vis diffuse reflectance spectroscopy (UV–vis DRS) absorption spectra were recorded with a UV-2550 spectrophotometer, using BaSO_4 as a reference. The specific surface areas were measured at 77 K using a 3 H-2000PSI instrument and calculated by Brunauer–Emmett–Teller method. The contents of C and N in the samples were analyzed by the elemental analyzer (vario EL II, Elementar, Germany).

2.3. Photocatalytic activity

The catalysts were evaluated by photocatalytic decolorization of RhB under irradiation of visible light ($\lambda > 420 \text{ nm}$) using a 300 W tungsten halide lamp as light source with a cut-off filter above the reactor. For the degradation of RhB, 0.050 g of the prepared photocatalyst was dispersed in 50 mL RhB solution (5 mg L^{-1}). Before illumination, the suspensions were stirred for 1 h in dark in order to reach an adsorption–desorption equilibrium between the photocatalyst and RhB. Then, the solution was exposed to visible light irradiation under magnetic stirring. At certain intervals, 4 mL solution was sampled.

3. Results and discussion

3.1. Characterization of the photocatalysts

The XRD patterns of the prepared $g\text{-C}_3\text{N}_4$, CN600-0.5 were displayed in Fig. 1. The XRD result shows that both samples contain the main structure of $g\text{-C}_3\text{N}_4$, with peaks at around 13.1° and 27.4°, and without any other impure phase. The former weaker peak corresponds to the in-planar structural packing motif of $g\text{-C}_3\text{N}_4$, such as the distance of the nitride pores. The latter peak around 27.4° is attributed to the (002) planes of $g\text{-C}_3\text{N}_4$, which also reveals the distance between the $g\text{-C}_3\text{N}_4$ layers is 0.326 nm [35]. Interestingly, the detailed analysis shows that the latter peak of CN600-0.5 shifts from 27.4° to 27.7°, corresponding to a decrease in the interplanar stacking distance from 0.326 to 0.322 nm. This phenomenon could be interpreted as the improvement of the interlayer stacking order in the second heating process. On the other hand, the former peak intensity of CN600-0.5 decreases. This could be attributed to that annealing may partially destroy the structure to form N-vacancy in the $g\text{-C}_3\text{N}_4$ and reduce the long-range order of the motif.

Fig. 2 shows the FTIR spectra of the pristine $g\text{-C}_3\text{N}_4$ and CN600-0.5 samples. The FTIR spectra illustrate that CN600-0.5 contains the same structure as the pristine $g\text{-C}_3\text{N}_4$. Both samples show the typical IR patterns of graphitic carbon nitride. The peak at the region 810 cm^{-1} can be attributed to the characteristic breathing mode of triazine units. Additionally, the other several

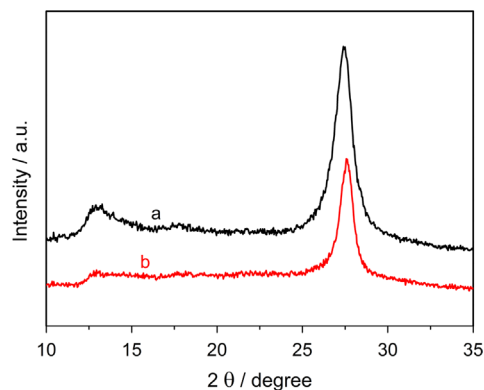


Fig. 1. XRD patterns of (a) $g\text{-C}_3\text{N}_4$, and (b) CN600-0.5.

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