Applied Catalysis B: Environmental 227 (2018) 541–547

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Facile two-step treatment of carbon nitride for preparation of highly efficient visible-light photocatalyst

Ningxin Jiang[a,b], Hongjia Wang[a,b], Yidan Luo[a,b], Shuohan Yu[a,b], Annai Liu[a,b], Weixin Zou[a,b], Fei Gao[a,b,*], Lin Dong[a,b,*]

[a] *Jiangsu Key Laboratory of Vehicle Emissions Control, School of the Environment, Center of Modern Analysis, Nanjing 210093, PR China*
[b] *Key Laboratory of Mesoscopic Chemistry of Ministry of Education, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China*

ARTICLE INFO

Keywords:
Graphitic carbon nitride
Ammonia solution
Two-step treatment
Photocatalyst

ABSTRACT

Tailoring the microstructure of graphitic carbon nitride (GCN) is an effective way to improve its photocatalytic activities. Protonation of GCN has been extensively studied, while few researches focused on modifying GCN with alkali. Herein, we report a facile two-step hydrothermal-calcination method to modify GCN. After hydrothermal treatment with ammonia solution and subsequently calcination under argon atmosphere, the as-synthesized GCN-xh-Ar (x stands for hydrothermal time) samples exhibit drastically improved photocatalytic activities towards photocatalytic degradation of RhB and evolution of hydrogen. The GCN-2h-Ar sample shows the highest hydrogen evolution rate of 736 μmol h^{-1} g^{-1}, which is nearly 11 times of pristine GCN (67 μmol h^{-1} g^{-1}). The improved activities of samples can be attributed to the higher surface area, larger pore volume and enhanced visible light absorption. This approach sheds light on the synthesis of highly efficient photocatalysts.

1. Introduction

Graphitic carbon nitride (GCN) is known as a metal-free polymer semiconductor which can be served as a catalyst for water splitting, pollutant photodegradation, CO_2 photoreduction and nitrogen fixation [1–5]. As a promising photocatalyst, it has several interesting properties including active in visible light region, stable and environmental friendly. However, the disadvantages of GCN are also conspicuous: the low surface area, low absorbance of visible light, and fast recombination of photogenerated electrons and holes [6]. Thus, numerous strategies have been employed to improve the efficiency of GCN such as nanoarchitecture design, functionalization of GCN, formation of proper heterostructures and loading with metal cocatalysts [7–12].

Various researches focused on the nanostructure design of GCN to tailor the interlayer relationship and structural properties of GCN. The band gap structure, surface area, porosity, morphology, structure and size of GCN can be easily modified with proper treatments and designs [10,13–15]. Most studies focused on one step treatment of GCN such as hydrothermal, protonation, calcination and sonication methods, which can easily tune some properties and thus improve the photocatalytic activities of carbon nitrides [16–26]. Hydrothermal method is an effective way to modify GCN. A lot of materials such as $H_3PW_{12}O_{40}$ [27], NiS [28], Bi_2WO_6 [29] and $BiVO_4$ [30] has been fabricate with carbon nitride to build efficient heterojunction with hydrothermal methods. Hydrothermal treatment of pure carbon nitride in certain solution including water [16,17], sodium hydroxide [18] hydrogen peroxide solution [24] and the ammonia thiosulfate solution [25] is another way to get effective photocatalyst. However, few research use solution with high pH to modify the carbon nitride which might because the hydroxide ions will break the C—N—C bonds and decrease the polymerization degree of carbon nitride [18]. Thus, it is interesting to find a proper way of improving activities of carbon nitride with alkaline treatment.

Recently, some researchers focused on two-step methods which contain some of these one-step treatment to further improve the activities of GCN materials [23,31–39]. Typically, the first step aims at designing highly ordered nanoarchitecture by treating GCN or molecules rich in carbon and nitrogen such as melamine under hydrothermal conditions or heating in certain solutions. The second step is mostly calcination of GCN under different atmosphere to synthesis GCN with specific structure, higher polymerization degree and extended visible light absorption range. For example, the highly ordered layered porous GCN structures with higher activities towards photodegradation of RhB were prepared with an acetic acid induced two-step method [33]. Sulfuric acid can also be used as solvent in the first step and subsequent calcination of product can generate good photocatalysts [37,38]. However, it remains a challenge to synthesize GCN with proper two-

---

* Corresponding authors at: Jiangsu Key Laboratory of Vehicle Emissions Control, School of the Environment, Center of Modern Analysis, Nanjing 210093, PR China.
E-mail addresses: gaofei@nju.edu.cn (F. Gao), donglin@nju.edu.cn (L. Dong).

https://doi.org/10.1016/j.apcatb.2018.01.056
Received 4 September 2017; Received in revised form 10 January 2018; Accepted 23 January 2018

step treatment because most two-step methods use expensive and harmful reagents and the activities of catalysts are relatively low. Also, most methods employed acid in the first step while few research used basic solution in the first-step treatment. Thus, using alkaline treatment as the first step and calcinating the product under certain atmosphere might be a good way to obtain an active photocatalyst.

In this work, ammonia solution induced two-step hydrothermal-calcination method was developed for the preparation of highly efficient carbon nitride photocatalyst. After hydrothermal treatment of GCN in ammonia solution, the mixtures of melem hydrate hexagonal prisms and high-surface-area porous GCN are generated. The subsequent calcination process leads to the formation of GCN-xh-Ar (x stands for the hydrothermal time) composed of two types of carbon nitride. The two-step treatment provides the products with high surface area, large pore volume and effective visible-light harvesting ability. Thus, the as-synthesized product exhibits outstanding activities for photocatalytic production of H_2 and photodegradation of rhodamine B (RhB) under visible light irradiation.

2. Experimental sections

2.1. Preparation of catalytic materials

Bulk GCN was prepared by condensation of 10 g dicyandiamide in a crucible with a cover at 550 °C for 4 h with a ramping rate of 2.3 °C min^{-1} in the air in a muffle furnace. The product was well grinded in an agate mortar and denoted as GCN-pure. Hydrothermal treatment in ammonia solution was performed as follows. 2.0 g GCN-pure and 25 mL saturated ammonia solution were mixed in a 50 mL Teflon-lined stainless-steel autoclave. The autoclave was heated at 150 °C for different time. The product was collected after the reaction and washed with deionized water several times and ethanol one time. The product was denoted as GCN-xh (x refers to different hydrothermal time) after drying in an oven at 100 °C for 12 h 0.5 g GCN-xh was put into a porcelain boat. The boat was placed in the tube furnace and heated to 600 °C under argon with a ramping rate of 3 °C min^{-1}. The final product was denoted as GCN-xh-Ar. The sample directly calcinated under argon was designated as GCN-Ar. The synthesis process is illustrated in Fig. 1a.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on an XRD-6000 X-ray diffractometer (Shimadzu) using Ni-filtered Cu Kα radiation ($\lambda = 0.15418$ nm). Fourier transform infrared (FT-IR) spectra were collected on a Nicolet iS10 spectrometer. Scanning electron microscopy (SEM) experiments were performed on S-3400N II electron microscope. Transmission electron microscopy (TEM) images were taken on a JEM-2100 instrument at an acceleration voltage of 200 kV. Brunauer-Emmet-Teller (BET) surface areas were measured by nitrogen adsorption at 77 K using an ASAP2020 physical adsorption instrument (Micromeritics). UV–vis diffuse reflectance spectroscopy (UV–vis DRS) were recorded by a Shimadzu UV-3600 spectrophotometer with $BaSO_4$ as reference. X-ray photoelectron spectra (XPS) analysis was performed on a PHI 5000 Versa Probe system with monochromatic Al Kα radiation (1486.6 eV) operating at an accelerating power of 15 kW. The sample charging effects were compensated by calibrating all binding energies (BE) with the adventitious C 1s peak at 284.6 eV. Elemental analysis was performed on a CHN-O-Rapid instrument (Heraeus). The photoluminescence spectra and time-resolved photoluminescence emission spectra (335 nm excitation) were measured at room temperature with an FLsp-920 (Edinburgh) spectrophotometer.

2.3. Photocatalytic evaluation

The degradation of RhB was evaluated in aqueous solution under visible light irradiation. The visible light ($\lambda \geq 420$ nm) was provided by 500 W metal halide lamp with a 420 nm cut-off filter. 50 mg catalyst was added to 50 mL RhB (10 mg L^{-1}) solution. Before irradiation, the suspension was stirred for 30 min in the dark to achieve the adsorption-desorption equilibrium between RhB and the catalysts. When the light was on, approximately 3 mL suspension was obtained from solution at fixed intervals (10 min) and removed catalysts after centrifugation. The concentration of RhB was analyzed by UV–vis spectrophotometer according to its absorbance at 554 nm.

The photocatalytic hydrogen generation reactions were carried out in a top-irradiation vessel connected to a gas-closed glass system under the irradiation of 300 W Xe lamp equipped with a 420 nm cut-off filter. Typically, 50 mg catalyst was dispersed in 100 mL aqueous solution containing 90 mL deionized water and 10 mL triethanolamine as electron donor. Proper amount of H_2PtCl_6 aqueous solution was added as the precursor of Pt which was in-situ reduced during the reaction (3 wt % Pt). The temperature of solution was maintained at 6 °C during the experiment. The reactor was sealed and evacuated for 30 min before reaction. The amount of hydrogen gas was determined by a gas chromatograph.

3. Result and discussion

3.1. Morphology and structural characterization

The structures of as-obtained GCN-xh and GCN-xh-Ar were verified by X-ray diffraction (XRD, Fig. 2a) and Fourier transform infrared (FT-IR, Fig. 2b). The XRD patterns of GCN-xh show both melem hydrate and GCN diffraction peaks which indicate the formation melem hydrate in samples after hydrothermal treatment [40]. The FT-IR spectra of

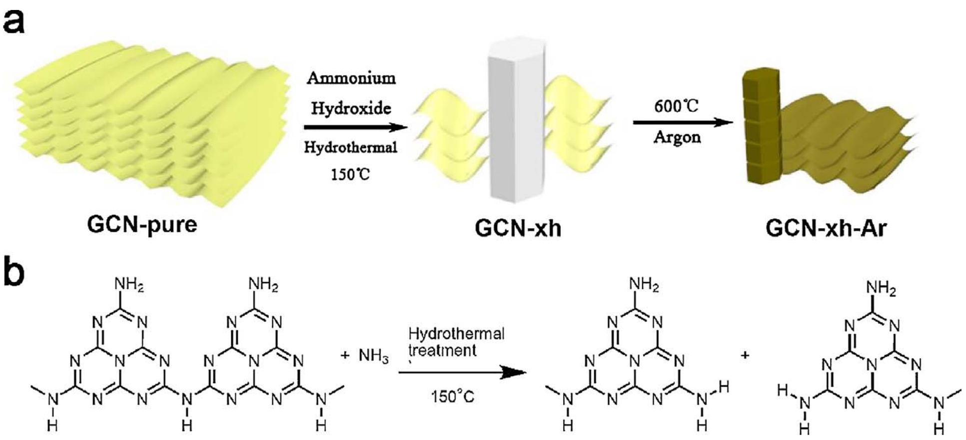

Fig. 1. a) Schematic model of formation of GCN-xh-Ar. b) Reaction scheme of aminolysis of GCN.