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Original Research Paper

# A template-free method to synthesize porous G-C<sub>3</sub>N<sub>4</sub> with efficient visible light photodegradation of organic pollutants in water

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## ABSTRACT

Porous graphitic carbon nitride with a high surface area was successfully synthesized without using any template or other substances like metals, just by placing melamine powder into a muffle furnace which was heated to 550 °C in advance. To evaluate the structure, morphology, and optical properties, the high performance g-C<sub>3</sub>N<sub>4</sub> (HPCN) was analyzed by XRD, SEM-EDX, TEM, N<sub>2</sub> physisorption, FT-IR analysis, UV-Vis DRS, PL, and Zeta potential. HPCN was able to completely degrade rhodamine B under visible light with the rate constant of 0.086 min<sup>-1</sup>, which is 3.5 times higher than the traditional g-C<sub>3</sub>N<sub>4</sub>. The possible mechanism of RhB photodegradation was discussed in detail, which illustrated the reaction is performed in acidic media much better than neutral and basic solutions, and ·O<sub>2</sub><sup>-</sup> and h<sup>+</sup> are the key reactive species during the reaction. Moreover, the stability of the photocatalyst was investigated and turned out its photocatalytic activity has not considerably changed after 6 cycles, so it was a highly stable photocatalyst.

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## 1. Introduction

Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), a metal-free semiconductor, has earned worldwide attention for its numerous advantageous such as photocatalysis [1], adsorption [2], sensor [3], solar cell [4], battery [5], catalysis [6]. G-C<sub>3</sub>N<sub>4</sub> as a photocatalyst has been applied for water splitting and H<sub>2</sub> evolution [7–10], pollutant degradation [11–14], CO<sub>2</sub> reduction [15,16], disinfection [17,18], etc. These wide variety of applications stem from its excellent electronic and optical properties with a desired band gap of 2.7 eV, high physicochemical stability, 2D layered structure, low price, clean and nontoxicity materials, and simple synthesis method with cheap precursors [19]. In spite of all these excellent features, g-C<sub>3</sub>N<sub>4</sub> suffers from rapid recombination rate of photoinduced e<sup>-</sup> and h<sup>+</sup>, low adsorption efficiency of solar light (only wavelengths below 460 nm) and low surface area of below 10 m<sup>2</sup> g<sup>-1</sup>, which limit its industrial applications. Therefore, g-C<sub>3</sub>N<sub>4</sub> needs to be modified to become much more helpful for environmental issues. Numerous efforts have been done by researchers to meet these needs. Synthesis of nanostructured g-C<sub>3</sub>N<sub>4</sub>, like nanotubes [20], nanosheets [21], and nanospheres [5] has been a promising method to improve its activity, but the yield of these methods are too low to be applicable. Preparation of mesoporous carbon

nitride is an excellent way to enhance its surface area with supplying pores inside the structure [22–26]. It obtains by using different kinds of templates, which create some problems like non-environmental feature of removing hard templates, and unwanted residuals into the framework of carbon nitride by using soft templates. Porous morphology could considerably raise the photoactivity of g-C<sub>3</sub>N<sub>4</sub> due to the greater number of surface active sites in contact with the pollutants [27]. Some scientists try not to use templates to synthesize porous g-C<sub>3</sub>N<sub>4</sub> with enhanced surface area, that was reported here briefly in following. Pretreatment of the precursors, or treatment of bulk g-C<sub>3</sub>N<sub>4</sub> with acids, or other substances is becoming an interesting way to make porous structure [28–32]. Recently, Niu et al. has found a new way of post thermal treatment to introduce some defects into graphitic carbon nitride [33]. Although without using any other substances it was effective, its surface area was still too low (21.6 m<sup>2</sup> g<sup>-1</sup> for the optimized product).

In this study, a really facile but highly efficient template-free method was introduced to synthesize a high performance g-C<sub>3</sub>N<sub>4</sub> as a photocatalyst active in visible light just by placing the precursor into a muffle furnace that was heated to the temperature 550 °C in advance. This new technique could produce porous g-C<sub>3</sub>N<sub>4</sub> with high surface area. The performance of the prepared g-C<sub>3</sub>N<sub>4</sub> in photodegradation of organic pollutants was researched in RhB degradation under visible light, and its stability and mechanism were evaluated in details.

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## 2. Experimental

Characterization part is provided in supplementary data file.

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.appt.2018.07.027>.

### 2.1. Materials and preparation procedures

Melamine and rhodamine B (RhB) were purchased from Merck and Sigma-Aldrich respectively. 4 g of melamine powder was distributed into a ceramic bowl with a lid. The furnace was heated to a temperature of 550 °C, and then the bowl was placed into the furnace at this temperature in air and remained there for 4 h. After that it was naturally cooled to room temperature and was crushed into fine powder for further use. This high performance graphitic carbon nitride was called HPCN. For comparison, the bulk g-C<sub>3</sub>N<sub>4</sub> was synthesized according to its common preparation method; so as to melamine was heated in air to 550 °C for 4 h with ramping rate of 3 °C min<sup>-1</sup>.

### 2.2. Photocatalytic test

To evaluate the performance of HPCN in photodegradation of organic pollutants in water, RhB was selected to be degraded under visible light. For photocatalytic experiment, a solution of RhB in water with concentration of 5 ppm was prepared. The solution pH was controlled by adding HCl and NaOH solutions of 0.1 M. 40 mg of the photocatalyst was dispersed in the solution and was placed in dark while stirring for 30 min to reach the adsorption-desorption equilibrium. Then the suspension was irradiated under a 300 W halogen lamp (Osram) with a UV filter, and was hold at room temperature. At various breaks, 3 mL of the suspension was collected, centrifuged for 5 min, and the concentration was monitored by UV-Vis spectrophotometer model Raleigh UV-1600 at 554 nm wavelength.

## 3. Results and discussion

### 3.1. Characterization

To investigate the crystal structure of HPCN, XRD patterns were provided in Fig. 1. The diffraction peaks of (0 0 2) and (1 0 0) which are characteristics of graphitic carbon nitride structure, were the same as the pristine g-C<sub>3</sub>N<sub>4</sub> (CN), that reflected the structure of

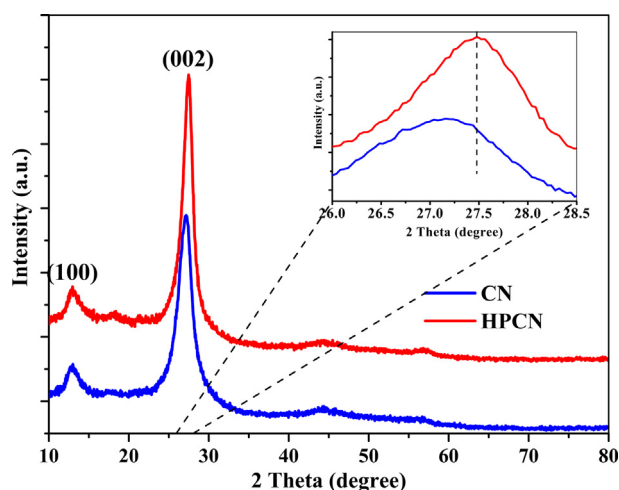


Fig. 1. XRD patterns of CN and HPCN.

g-C<sub>3</sub>N<sub>4</sub> were repeated in HPCN. However, the diffraction peak of (0 0 2) for HPCN shifted to upper angles (27.48° vs. 27.12°); It is contributed to decreasing the average interlayer distance in HPCN and a denser structure than CN [34]. Furthermore, the intensity of this diffraction peak enhanced for HPCN compared to CN, illustrating the more ordered structure for HPCN [35]. This ordered and compressed structure of HPCN referred to less defects. Hence, defects in photocatalysts structures may play the role of recombination centers for photoinduced electron and hole pairs, less defects in HPCN meant more separation of charge carriers and higher photocatalytic activity.

To investigate the morphology of HPCN, SEM and TEM images were provided as shown in Fig. 2. The SEM image of HPCN in comparison to CN showed some breakages and holes inside the structure which were induced by exposing melamine to a high temperature. These holes made a porous structure with greater surface area in the prepared sample. TEM images in Fig. 2c, d showed a structure containing flat sheets with irregular form. TEM image of HPCN (Fig. 2d) illustrated a porous morphology, but for CN the sheets were presented without any pores in it. Furthermore, the elemental composition of HPCN was then characterized by SEM-EDS, as shown in Fig. 2e, which proved that its structure included C, N, and O (the Au peak is related to its coating with Au). Compared to the bulk CN, more oxygen and less nitrogen atoms existed in the structure of HPCN. The more oxygen atoms in the structure instead of nitrogen could play the role of oxygen doping, and change the structural and electronic properties, so that it is able to delocalize the conjugated  $\pi$  electrons better.

As indicated in N<sub>2</sub> adsorption-desorption isotherms (Fig. 3) the surface area was increased from 11 m<sup>2</sup> g<sup>-1</sup> to 62 m<sup>2</sup> g<sup>-1</sup> for HPCN that was 5.6 times higher than the traditional g-C<sub>3</sub>N<sub>4</sub>. Besides, the total pore volumes reported by BJH method for CN and HPCN were 0.029 cm<sup>3</sup> g<sup>-1</sup> and 0.174 cm<sup>3</sup> g<sup>-1</sup> respectively, which confirmed the porous structure of HPCN. It can be found from the pore width distribution graph (Fig. 3 inset) that most of these pores were below 100 nm, that suggested the formation of nanoporous structure for HPCN.

The UV-Vis diffuse reflectance (DRS) and photoluminescence spectra were used to reach important data about optical properties consisting the absorption edge, band gap, and charge recombination of the HPCN, which are critical issues for determining the photocatalytic activity of a photocatalyst. DRS spectra of the samples and their graph of  $(\alpha h\nu)^2$  versus band gap energies, shown in Fig. 4a, indicated a slight enhancement in their band gap energies from 2.63 to 2.69 eV for the common g-C<sub>3</sub>N<sub>4</sub> and HPCN, respectively, that would be due to the porous structure of HPCN. In porous structures, the visible light may go through several reflections to reach the surface of the photocatalyst, which this phenomenon improves the energy efficiency of the visible light [36]. In fact, the enlarged band gap for HPCN might increase the redox efficiency of the photocatalyst. In PL analysis, as illustrated in Fig. 4b, the peak intensity of HPCN at 442 nm was decreased in comparison to CN, with characteristic peak around 447 nm, which was contributed to more separation of photogenerated electron-hole pairs. The more separation of the photoinduced charges can be attributed to the in-plane holes which could simplify the mass transfer and enhance the mobility of the photogenerated electrons and holes. In fact, the new method, reported in this work, could obtain g-C<sub>3</sub>N<sub>4</sub> with a slight less charge carrier recombination, and therefore more photocatalytic efficiency.

FTIR spectra of CN and HPCN were shown in Fig. 5. As can be seen, all of the peaks contributed to g-C<sub>3</sub>N<sub>4</sub> including stretching vibration of C–N and C=N (1245, 1322, 1410, 1564, and 1636 cm<sup>-1</sup>) [37], triazine breathing mode (808 cm<sup>-1</sup>), and NH<sub>2</sub> or NH as defects of aromatic rings in g-C<sub>3</sub>N<sub>4</sub> (3000–3400 cm<sup>-1</sup>) [38], were clear in both spectra of CN and HPCN, and there was no difference

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