



## Research paper

## Morphology and defects regulation of carbon nitride by hydrochloric acid to boost visible light absorption and photocatalytic activity

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## ABSTRACT

In this work, a hydrochloric acid assisted exfoliation approach to prepare the ultrathin carbon nitride (U-CN) nanosheet and to regulate its morphology and defects was reported. Based on moderate oxidation of hydrochloric acid, bulk carbon nitride (BCN) was just right broken into small pieces with protonation, which is beneficial to the exfoliation of BCN to U-CN nanosheets. Meanwhile, the main structure of CN do not be destroyed. Moreover, hydrochloric acid gives priority to cleave the bridging N atoms with rich elections, leading to the formation of the favorable defects and improving its photocatalytic performance. The obtained U-CN nanosheets prepared in a suitable HCl concentration exhibits enhanced photocatalytic efficiency for hydrogen evolution and Rhodamine B degradation under visible light. Such U-CN nanosheets with simple preparation, low cost, good yield and good photocatalytic activity might shed light on an acid-assisted method for developing high-performance CN photocatalysts.

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## 1. Introduction

With the increasingly serious global energy crisis and environmental contamination, photocatalysis technology has become a popular topic, which could address those problems via water splitting, carbon dioxide conversion, and water purification [1–7]. Titanium dioxide (TiO<sub>2</sub>), which has promising energy and environmental applications, is the widely studied photocatalyst owing to its low cost, high stability, and excellent recyclability [7–10]. However, high recombination rate of photo-induced charge carriers and the large bandgap (3.2 eV for anatase) of TiO<sub>2</sub> have greatly limited its widespread applications [3,11–13]. Recently, graphitic carbon nitride (*g*-C<sub>3</sub>N<sub>4</sub>), a metal-free polymer, has gained considerable popularity, due to its visible-light-driven bandgap, proper band edges, and environmental benignity [14–17]. However, the photocatalytic activity of BCN synthesized by thermal condensation is poor, which make it far from practical application [18]. Many efforts have been contributed to enhancing the photocatalytic activity of BCN, including metal and metal-free element doping [19,20],

transition metal heterostructure formation [16,21–25], and nanostructure construction [26].

Recently, various nanostructures have been designed and prepared successfully, such as nanospheres [27], nanomeshes [26], and nanosheets [28]. They always have an increased specific surface area, a promoted ultrahigh charge carrier mobility and an enhanced energy band structure, which could effectively improve photocatalytic activities of CN [29,30]. CN nanosheet, the simplest and widely applied structure, have been of great interest to researchers in past few decades [26,31,32]. Niu et al. prepared the CN nanosheets by the thermal etching of BCN in static air [29]. The resultant nanosheets possess not only a large specific surface area but also an increased bandgap, an improved electron transport ability and a prolonged lifetime of charge carriers as a result of the quantum confinement effect. When the surface energy of BCN matches that of the solvent, liquid exfoliation could be used for preparing CN nanosheets [31]. Zhang et al. theoretically calculated the surface energy of *g*-C<sub>3</sub>N<sub>4</sub> (115 mJ/m<sup>2</sup>), which matches well with that of water (102 mJ/m<sup>2</sup>) [33]. CN nanosheet could be obtained via water intercalation exfoliation method. However, the yield of the obtained CN nanosheets is relative low, due to great van der Waals force between the large layers of BCN. So the yield of CN nanosheets could be improved via decrease the BCN size.

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Acid-assisted exfoliation of BCN has been a common method to prepared CN nanosheets [28,32,34]. The acid could cleave BCN into small pieces and protonate the layers [34]. The protonated BCN with smaller size not only induces electrostatic repulsion, provides better dispersion and a larger specific surface area, but also enables the adjustment of electronic band gaps and have higher ionic conductivity [19,23]. Zhou et al. propose CN layer can be cleaved by  $\text{H}_2\text{SO}_4$ , and various CN nanostructures including CN quantum dots, nanoleaves and nanorods could be facily prepared in different hydrolysis conditions [24]. However,  $\text{H}_2\text{SO}_4$  and sulphate radical formed by absorption of residual  $\text{SO}_4^{2-}$  in the CN possess strong oxidation. Besides, Zhang et al. found that the ionic conductivity and photoconduction of the CN solids have been improved after HCl treatment [35]. HCl possesses moderate oxidation, which is just right cleave the layer of BCN, so HCl is considered as an ideal candidate to control the structure and photocatalysis performance of the CN. However, the preparation of the ultrathin CN nanosheet by HCl and the influence of HCl concentration to the morphology of CN have not been reported.

Herein, U-CN nanosheets with enhanced photocatalytic activity were prepared by HCl-assisted hydrothermal exfoliation of BCN. In this exfoliation process, BCN was broken into small pieces by HCl, which is conducive to water intercalates, the disturbance of van der Waals force between the layers and the formation of U-CN nanosheets. Meanwhile, HCl solution could introduce favorable defects of CN nanosheets which could boost its photocatalytic performance. Moreover, the HCl concentration is a key factor to the exfoliation of BCN, due to its influence to the morphology regulation and the formation of the favorable defects. Therefore, the U-CN nanosheets prepared in a suitable concentration exhibit enhanced photocatalytic efficiency for hydrogen evolution and Rhodamine B degradation under visible light, which might indicate an acid-assisted method for developing high-performance CN photocatalysts.

## 2. Experimental section

### 2.1. Materials

Melamine ( $\text{C}_3\text{H}_6\text{N}_6$ , 99.0%) was purchased from Sigma-Aldrich. Hydrochloric acid (HCl, 37%) was obtained from the Sinopharm Chemical Reagent Co., Ltd. All chemicals are of analytical grade and were used as received without further purification. Doubly distilled water was used throughout the experiments.

### 2.2. Synthesis of photocatalyst

The synthesis of BCN was according to a previously reported [29]. The CN nanosheets were prepared by exfoliation of BCN as followed: BCN (1 g) and HCl solution (50 mL, 6 M) were added into a 100 mL of teflon-lined stainless steel autoclave and heated to  $120^\circ\text{C}$  for 4 h. After cooled to room temperature, the photocatalyst was obtained by centrifugation-dispersion-ultrasonication cycles and dried at  $80^\circ\text{C}$  under vacuum overnight, which was denoted as U-CN-6. Other samples were prepared by the same method with different initial concentration of HCl (0, 3, and 9 M), and denoted as U-CN-0, U-CN-3, and U-CN-9, respectively.

### 2.3. Characterization

X-ray diffraction (XRD) patterns of the as-prepared samples were recorded at room temperature by a Bruker D8 Advance X-ray diffractometer. Fourier transformed infrared (FT-IR) spectroscopy were recorded by a Nicolet IS 10 FT-IR spectrometer, using the KBr wafer technique. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCA Lab220i-XL electron spectrometer

from VG Scientific using 300 W Al K $\alpha$  radiation. Transmission electron microscope (TEM) images of the as-prepared samples were measured by a Hitachi HT 7700 electron microscope operated at an accelerating voltage of 100 kV. The thickness of samples were measured by atomic force microscopy (AFM, Digital D3000). The UV–vis diffuse reflectance absorption spectroscopy (DRS) was recorded on a UV–vis spectrophotometer (Hitachi, UH4150) equipped with an integrated sphere attachment, and  $\text{BaSO}_4$  was used as a reference. Photoluminescence (PL) spectroscopy of samples was measured on an F-4600 FL spectrophotometer at room temperature (excitation wavelength at  $\lambda = 380$  nm).

### 2.4. Photoelectrochemical measurement

The electrochemical experiments were performed under a standard three-electrode system, with a platinum sheet used as the counter electrode, F-doped stannic oxide (FTO) glass ( $1.0 \times 1.0$  cm $^2$ ) as the working electrode and Ag/AgCl (saturated KCl solution) as the reference electrode. A bias potential of 0.5 V versus Ag/AgCl was used in the experiments, sodium sulfate solution ( $\text{Na}_2\text{SO}_4$ , 0.1 M, pH=7) was used as the electrolyte and a 300 W Xenon lamp (PLS-SXE 300C (BF), PerfectLight, Beijing) with an optical filter ( $\lambda > 420$  nm) was used as the visible-light source. The Mott-Schottky plots were obtained in the dark at 1000 Hz.

### 2.5. Photocatalytic activity

Photocatalytic hydrogen evolution reactions were recorded by a photocatalysis online analyze system (Labsolar-III, PerfectLight, Beijing). Briefly, 50 mg of photocatalysts were dispersed in 100 mL of 10 vol% triethanolamine (TEOA) aqueous solution, 3 wt% Pt was in-situ photodeposited on the surface of photocatalysts by adding  $\text{H}_2\text{PtCl}_6$ . A 300 W Xenon lamp with an optical filter ( $\lambda > 420$  nm) was used as the visible light source. The measured average incident power of light was about  $0.158$  W cm $^{-2}$  and the diameter of the light source is 6.3 cm. Before visible-light irradiation, the suspension was fully degassed to remove air. The amount of hydrogen produced was quantified by the gas chromatograph (GC D7900P, TCD detector, Ar as a carrier gas, 5 Å molecular sieve column, Shanghai Tech comp).

## 3. Results and discussion

U-CN nanosheets were prepared through a HCl-assisted hydrothermal exfoliation method, as showed in Scheme 1. The HCl concentration is an important factor to regulate the morphology and the defects of CN. With the HCl concentration increasing, the cleavage is stronger, and more defect points are formed. But the introduction of more oxygen-containing groups lead to the stronger forces between the layers, which hinder the exfoliation of BCN. When the HCl concentration is a suitable amount, it is beneficial to the formation of CN nanosheets and the favorable defect. The crystal structures of the U-CN were characterized by XRD, as shown in Fig. 1. Two obvious characteristic peaks in BCN pattern were observed at  $12.6^\circ$  and  $27.1^\circ$ , indexed as (100) and (002) peak, respectively [35]. The (100) peak can be assigned to the in-plane structural packing motif of tris-triazine units, while the (002) peak is ascribed to the interlayer stacking of aromatic segments [36,37]. However, for all U-CN, the (100) peak becomes less pronounced, which indicates the planar size of the layers decreased during hydrothermal exfoliation of BCN [29]. The (002) peak of U-CN-0 is shifted from  $27.1^\circ$  to  $27.3^\circ$  and U-CN-3 to 9 is shifted to  $27.5^\circ$ , indicating a decreased gallery distance between layers [28]. Because the layers of BCN are potentially undulated, the decreased layer size caused by HCl cleavage lead to the occurrence of layer planarized [5,28]. As shown in Fig. S1, the IR spectrums of all samples

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